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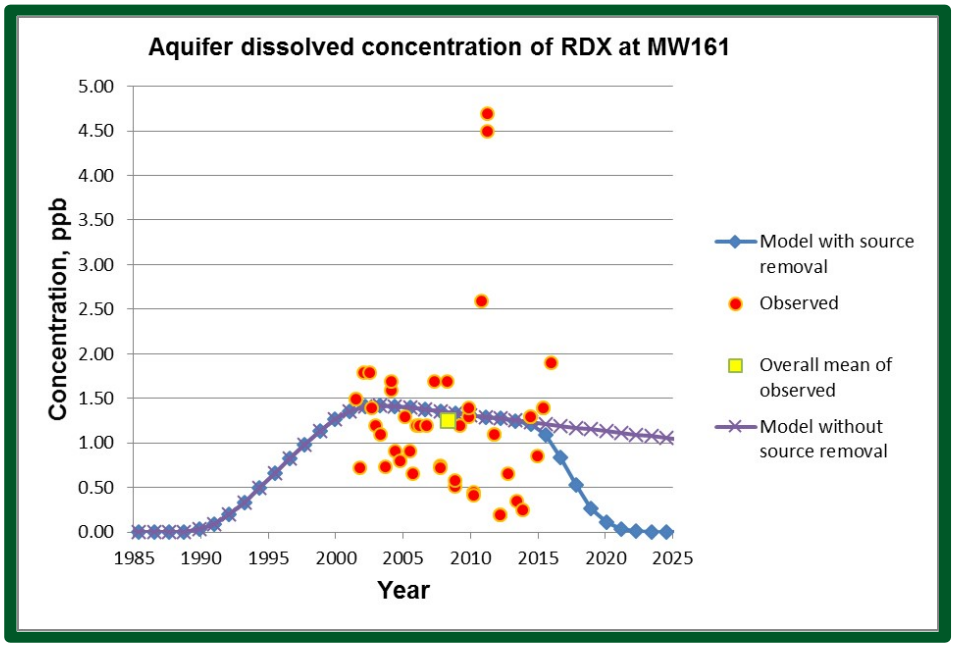

Field Demonstration and Validation of TREECS™ and CTS for the Risk Assessment of Contaminants on Department of Defense (DoD) Ranges

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14. ABSTRACT
The Training Range Environmental Evaluation and Characterization System (TREECS™) was developed to forecast the fate of and risk from munitions constituents (MC), such as high explosives (HE) and metals, within and transported from firing/training ranges to surface water and ground-water. The Chemical Transformation Simulator (CTS) was developed by the U.S. Environmental Protection Agency to provide physicochemical properties of complex organic chemicals. TREECS™ requires such proper-ties for predicting environmental fate of MC. This study validated the capability of TREECS™ and CTS to predict MC (HE RDX) concentrations in receiving waters down-gradient of training/firing ranges for three installations.

15. SUBJECT TERMS
Artillery Impact Area, Ammonium perchlorate, Adaptive Risk Assessment Modeling System, Chemical Abstract Service, Conceptual Site Model, Data for Environmental Modeling, Emerging contaminant, explosives ordnance disposal, High Explosives, Insensitive munitions, nitroguanidine, organic carbon, Small Arms Firing Ranges, rainfall factor in the USLE

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ACRONYMS AND ABBREVIATIONS

AFCEE	Air Force Center for Environmental Excellence
AIA	Artillery Impact Area
ECB	Environmental Chemistry Branch
AOI	Area of Interest
AMP	Arcadis – Malcolm Pirnie
AP	Ammonium perchlorate
ARAMS	Adaptive Risk Assessment Modeling System
ARCDB	Army Range Constituent Database with TREECS™
ATC	U.S. Army Aberdeen Test Center
bgs	below ground surface
BMP(s)	Best Management Practice(s)
C	crop management factor in the USLE
C4	HE consisting of RDX and plasticizers
CAS	Chemical Abstract Service
CBA	Cost Benefit Analysis
CL-20	IM explosive component, hexanitrohexaazaisowurtzitane (HNIW)
CMS	Contaminant Model for Streams
CN	curve number in the SCS curve number method for computing runoff
CON	Certificate of Networthiness
CSM	Conceptual Site Model
CTS	Chemical Transformation Simulator developed by EPA
D4EM	Data for Environmental Modeling
Demo	Demolition area
DNAN	2,4-dinitroanisole
DoD	U.S. Department of Defense
DODIC	Department of Defense Identification Code
EC(s)	Emerging contaminant(s)
EFS	Environmental Fate Simulator
EL	ERDC Environmental Laboratory
EOD	explosives ordnance disposal
EPA	U.S. Environmental Protection Agency
EPI	Estimation Program Interface
EPED	Environmental Processes and Effects Division
EQT	U.S. Army Environmental Quality Technology
ERDC	U.S. Army Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
FRAMES	Framework for Risk Analysis in Multimedia Environmental Systems
GIS	Geographical Information System

GUI	Graphical User Interfaces
HE	High Explosives
HGCT	TREECS™ Hydro-Geo-Characteristics Toolkit
HLC	Henry's Law Constant, units of atm-m^3/mole
HNIW	hexanitrohexaazaiso-wurtzitane
IM	Insensitive munitions
LCL	lower confidence limit for uncertainty analysis
LeC	Las Flores loamy fine sand soil class for ZIA, Camp Pendleton
LS	length-slope-gradient factor in the USLE
MC	Munitions Constituent
MCB	Marine Corps Base
MENA	1.2-methoxy-5-nitroaniline
MEPAS	Multimedia Environmental Pollutant Assessment System
MIDAS	Munition Items Disposition Action System
MMR	Massachusetts Military Reservation
MSL	Mean Sea Level
N	Nitrogen
NCEI	National Centers for Environmental Information of NOAA
NOAA	National Oceanic and Atmospheric Administration
NQ	nitroguanidine
NSN	National Stock Number
NTO	3-nitro-1,2,4-triazol-5-one
OC	organic carbon
ORAP	U.S. Army Operational Range Assessment Program conducted by Army and Air Force
P	conservation practice factor in the USLE
PAL(s)	protective action limit(s) for protection of environmental health in various media
ppb	parts per billion as concentration of a constituent in water, same as µg/L
QSAR	Quantitative Structure Activity Relationship
R	rainfall factor in the USLE
RDX	Royal Demolition Explosive, a high explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine
REVA	Range Environmental Vulnerability Assessment conducted by Marine Corps
RMUS	DoD Range Munitions Use Subcommittee

RSEPA	Range Sustainment Environmental Program Assessment conducted by Navy
RTC	range and training complex of USMA
SAFR	Small Arms Firing Ranges
SCS	Soil Conservation Service of the U.S. Department of Agriculture
SERDP	Strategic Environmental Research and Develop Program
SPARC	SPARC Performs Automated Reasoning in Chemistry
TEST	Toxicity Estimation Software Tool
T/E	Threatened and Endangered
TNT	HE trinitrotoluene
TREECS™	Training Range Environmental Evaluation and Characterization System
TSS	total suspended solids
UCL	upper confidence limit for uncertainty analysis
UI(s)	user interface(s) for entering and viewing model inputs
USGS	United States Geological Survey
USLE	Universal Soil Loss Equation
USMA	United States Military Academy
UXO	unexploded ordnance
WQCMB	Water Quality and Contaminant Modeling Branch
WSS	Web Soil Survey
WFF	water flux files within TREECS™
ZIA	Zulu Impact Area of Marine Corps Base Camp Pendleton

Symbols

f_{oc}	fraction organic carbon for TSS and benthic sediment
K_d	sorption distribution coefficient for partitioning an MC between soil or sediment particles and water, L/kg
K_{oc}	organic carbon normalized soil–water sorption partition coefficient, L/kg
K_{ow}	octanol–water sorption partition coefficient, mL/mL
K_{sat}	water-saturated hydraulic conductivity for groundwater flow, length/time
O	observed or measured data
P	model-predicted data
RR	result ratio, a metric for measuring model accuracy
RE	relative error, a metric for measuring model accuracy

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The work reported herein was conducted by Dr. Mark Dortch under contract to LimnoTech, Inc., which was under contract to the U.S. Army Engineer Research and Development Center (ERDC). Dr. Billy Johnson of the Water Quality and Contaminant Modeling Branch (WQCMB), Environmental Processes and Effects Division (EPED), Environmental Laboratory (EL) of ERDC was the project leader and federal point-of-contact for this work. Dr. Eric Weber of the Exposure Methods & Measurements Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency (EPA), was the technical point-of-contact for the Contaminant Transformation Simulator (CTS) that was developed by EPA and used as part of this project.

The study was conducted under the general direction of Dr. Dorothy Tillman, Chief, WQCMB; Warren Lorentz, Chief, EPED; and Dr. Beth Fleming, Director of the EL. Dr. Elizabeth Ferguson was Technical Director of military materials in the environment. Drs. Jeffery P. Holland and David W. Pittman served as the Director of ERDC. COL Bryan S. Green is currently the Commander and Executive Director. The points-of-contact for this project are provided in the Appendix.

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION: The objectives of this study were to demonstrate and validate the scientific approach of the Training Range Environmental Evaluation and Characterization System (TREECS™)[1] and the Chemical Transformation Simulator (CTS)[2] modeling systems to show that the performance is consistent, reliable, and cost effective and that TREECS™-CTS advances the ability to reliably quantify the potential of environmental risks of MC on, and down-gradient of DoD training and testing ranges. The TREECS™ and CTS were applied to three military training sites where the high explosive RDX has been detected in down-gradient receiving waters (i.e., groundwater or surface water). The three study sites were Demolition (Demo) Area 2 of the Massachusetts Military Reservation (MMR), MA., Artillery Impact Area (AIA) of the U.S. Military Academy (USMA), NY and Zula Impact Area (ZIA) of Marine Corps Base (MCB) Camp Pendleton, CA. The model for each site was validated against observed RDX concentrations, and an uncertainty analysis was conducted to evaluate the capability of the model to bracket observed data within the 95% confidence interval. The model was then applied for emerging constituent (EC) components of insensitive munitions (IM) at each study site to demonstrate the ability to evaluate EC fate relative to that of RDX. Then the model of each site was used to evaluate the effectiveness of three range management and/or remediation strategies (i.e., Best Management Practices, or BMPs) to reduce RDX concentrations to demonstrate the utility of TREECS™ for such purposes.

TECHNOLOGY DESCRIPTION: The TREECS™ was developed for the Army to forecast the fate of and risk from munitions constituents (MC), such as high explosives (HE) and metals, within and transported from firing/training ranges to surface water and groundwater. TREECS™ consists of contaminant fate/transport models for soil, vadose zone, groundwater, and surface water to forecast MC export from ranges and resulting concentrations in each medium. TREECS™ provides rapid assessment of off-site migration of MC and other contaminants to determine if and when range operations could pose risks to human and ecological receptors down-gradient of ranges. Additionally, TREECS™ can be used to evaluate Green Range Best Management Practice (BMP) alternatives to preserve human and ecological health. These predictive capabilities allow active evaluation and management of range environmental health rather than waiting on costly, periodic monitoring activities for information.

The CTS, previously called the Environmental Fate Simulator (EFS), was developed by the U.S. Environmental Protection Agency (EPA) to provide physicochemical properties of complex organic chemicals for both the parent chemical and predicted transformation products. The CTS has capabilities for estimating properties in the absence of experimentally obtained properties; thus, CTS can help fill data gaps for properties, particularly for emerging contaminants with limited experimental data. The physicochemical properties of the MC or contaminants (including emerging contaminants, or ECs) of interest are required for TREECS™ application. Although TREECS™ contains three separate databases for constituent physicochemical properties, there are data gaps within these databases that CTS can help fill.

[1] (http://www.erdc.usace.army.mil/Media/FactSheets/FactSheetArticleView/tabid/9254/Article/476659/training-range-environmental-evaluation-characterization-system.aspx)

[2] https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=310644

DEMONSTRATION RESULTS: Most of the project objectives' performance metrics were fully satisfied. The first quantitative metric on the ability of the model to accurately simulate the long-term fate of MC was graded as highly successful for all three study sites. The quantitative metric on the capability to assess the uncertainty of model inputs was graded as moderately successful due to the fact that the confidence bands did not include all observations. The sensitivity and uncertainty analysis feature of TREECS™ operated successfully and as intended. The failure to capture all of the observations within the uncertainty bands was attributed to hydrologic variations/uncertainty as well as the use of rather restrictive uncertainty limits for evaluating confidence bands. The first qualitative metric on the ability to set up a model with readily available data within 80 labor hours was successful for all three study sites. The second qualitative metric on reasonable training requirements has not been graded and is pending the execution of such training that is planned for 2017. The third qualitative metric on the use of TREECS™-CTS to evaluate range management and/or remediation strategies (BMPs) was successful for all three study sites. The fourth qualitative metric on the use of TREECS™-CTS to evaluate the fate of emerging MC was successful.

IMPLEMENTATION ISSUES: TREECS™-CTS should be an integral part of the successful administration of range sustainment programs to help avoid costly range compliance issues. There are really no major implementation issues associated with applying TREECS™. TREECS™ is client based so requires the System Administrator for installation. TREECS™ has an Army Certificate of Networthiness (CON). CTS is a web-based tool that is presently running behind EPA's firewall on a server. The CTS will be made fully available to the public in 2017.

Presently, there are no DoD or Army directives that require the use of TREECS™, and as a result, TREECS™ has not experienced the use that was originally envisioned during its developmental funding. Thus, the benefits of having a powerful forecast modeling tool such as TREECS™ are not being realized. TREECS™ is a mature, validated modeling tool that is fairly easy to apply relatively quickly. Qualified contract environmental personnel could be readily trained for applying TREECS™-CTS to provide the most expedient and cheapest route to range applications. TREECS™ will not be fully utilized without a requirement for implementation and application. An Army or DoD directive is needed to require such applications, which would provide cost savings, provide much improved site understanding and alternatives assessment, and help ensure range sustainment.

1.0 INTRODUCTION

1.1 BACKGROUND

The Training Range Environmental Evaluation and Characterization System (TREECS™)[3] was developed for the Army to forecast the fate of and risk from munitions constituents (MC), such as high explosives (HE) and metals, within and transported from firing/training ranges to surface water and groundwater. TREECS™ consists of time-varying contaminant fate/transport models for soil, vadose zone, groundwater, and surface water to forecast MC export from ranges and resulting concentrations in each medium. TREECS™ allows Department of Defense (DoD) training range managers and/or their environmental specialists to rapidly assess off-site migration of MC and other contaminants to determine if and when range operations could pose risks to human and ecological receptors down-gradient of ranges. Additionally, TREECS™ can be used to evaluate Green Range Best Management Practice (BMP) alternatives where concentrations are presently or are predicted in the future to exceed protective action limits (PALs) for human and ecological health. A detailed description of TREECS™, as well as its performance, are provided by Dortch et al. (2013a).

The physicochemical properties of the MC or contaminants (including emerging contaminants, or ECs) of interest are required for TREECS™ application. Such properties include, for example, molecular weight, solubility, solid phase density, sorption partitioning coefficients, Henry's constant, and degradation rates or half-lives. Although TREECS™ contains three separate databases for constituent physicochemical properties, there are data gaps within these databases.

The Chemical Transformation Simulator[4] (CTS), previously called the Environmental Fate Simulator (EFS), was developed by the U.S. Environmental Protection Agency (EPA) to provide physicochemical properties of complex organic chemicals for both the parent chemical and predicted transformation products. The CTS has capabilities for estimating properties in the absence of experimentally obtained properties; thus, CTS can help fill data gaps for properties, particularly for emerging contaminants with limited experimental data.

The CTS currently consists of three major components: (1) Chemical Editor that allows for the entry of the chemical of interest through either provision of the common name, smiles string notation, Chemical Abstract Service (CAS) registry number, or chemical structure; (2) Reaction Pathway Simulator, which is based on description of the environmental conditions (e.g., anaerobic vs. aerobic), provides the major transformation products based on the execution of reaction libraries for abiotic reduction, hydrolysis, aerobic biotransformation, and mammalian metabolism; and (3) Physicochemical Properties Calculators, which through access to SPARC (SPARC Performs Automated Reasoning in Chemistry), EPI (Estimation Program Interface) Suite, Toxicity Estimation Software Tool (TEST), and ChemAxon's plug-in calculators, provides the necessary physicochemical properties required for predicting environmental concentrations. Information from CTS is made available to TREECS™ to provide the constituent properties necessary for modeling contaminant fate.

[3] (http://www.erdc.usace.army.mil/Media/FactSheets/FactSheetArticleView/tabid/9254/Article/476659/training-range-environmental-evaluation-characterization-system.aspx)

[4] https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=310644

TREECS™ and CTS were applied jointly to three DoD study sites to validate the capability to predict MC concentrations in receiving waters down-gradient of training/firing ranges and to demonstrate the utility of these modeling systems for forecasting the fate of MC, as well as ECs, within and off site of DoD installations. The utility of the modeling system for evaluating BMPs was also demonstrated. The overall benefit of this work is to help transition these powerful tools to the appropriate user community so that they can be used to help ensure range compliance and sustainability into the future.

1.2 OBJECTIVE OF THE DEMONSTRATION

The objectives of this study were to demonstrate and validate the scientific approach of the TREECS™ and CTS modeling systems to show that the performance is consistent, reliable, and cost effective and that TREECS™-CTS advances the ability to reliably quantify the potential of environmental risks of MC on, and down-gradient of DoD training and testing ranges. The scope of the project included identifying active DoD training ranges, determining the nature and extent of MC, analyzing potentially complex exposure pathways, validating TREECS™-CTS to predict MC concentrations in receiving water, evaluating potential risk from exposure to MC, developing user guidance in applying the TREECS™-CTS for the environmental risk assessment, and providing transition and technology transfer for environmental specialists and range managers.

1.3 REGULATORY DRIVERS

All DoD ranges must be managed and operated to support their long-term viability and to meet the national defense mission while protecting the environment and human health (DoD Directives 3200.15 and 4715.11). In support of these policies, DoD Instruction 4715.14 requires all DoD Components to determine whether there has been a release or a substantial threat of a release of munitions constituents of concern from an operational range to an off-range area, to determine whether such a release creates an unacceptable risk to human health or the environment, and to enhance the Components' ability to prevent or respond to such a release. As a result, all DoD Components routinely perform range assessments. The Army and Air Force conduct the Operational Range Assessment Program (ORAP); the Marine Corps perform Range Environmental Vulnerability Assessment (REVA); and the Navy performs Range Sustainment Environmental Program Assessment (RSEPA).

As per DoD Instruction 4715.14, to ensure the long-term viability of operational ranges while protecting human health and the environment, all operational ranges must be periodically re-evaluated to determine if there is a release or substantial threat of a release of munitions constituents of concern from an operational range to an off-range area. This reevaluation shall occur at least every five years or whenever significant changes (e.g., changes in range operations, site conditions, applicable statutes, regulations, DoD issuances, or other policies) occur that affect determinations made during the previous assessment. Also, as part of this instruction – if data are insufficient to determine a potential MC source – receptor interaction, then further analysis, such as modeling, shall be conducted to evaluate this potential.

2.0 TECHNOLOGY

This section provides an overview of the technology that was demonstrated, including an in-depth explanation of the development.

2.1 TECHNOLOGY DESCRIPTION AND DEVELOPMENT

TREECS™ consists of time-varying contaminant fate/transport models for soil, vadose zone, groundwater, and surface water to forecast MC export from ranges and resulting concentrations in each medium. These disparate models are dynamically linked within a modeling framework, which is the Framework for Risk Analysis in Multimedia Environmental Systems (FRAMES)[5] (Whelan et al. 1997). The conceptual site model (CSM) as well as the schematic of TREECS™ model linkages is shown in Figure 1 for Tier 2. There are two levels of capability. Tier 1 consists of screening-level methods that assume highly conservative, steady-state MC loading and fate. Tier 1 requires minimal input data requirements and can be easily and quickly applied. Tier 2 provides time-varying analyses and solves mass balance equations for both solid and non-solid phase MC mass with dissolution. Additionally, MC residue loadings to the range soil can vary from year to year based on munitions use. Thus, media concentrations computed with Tier 2 should be closer to those expected under actual field conditions. There is also an Advanced Tier 2 option that allows the user to construct complex media pathways using the FRAMES CSM workspace (Figure 2). Developmental documentation reports for TREECS™ are provided by Dortch et al. (2009, 2011a, 2012, 2013a, 2013b), Dortch and Johnson (2012), Johnson and Dortch (2014a), and Dortch and Gerald (2015), as well as a user manual (Gerald et al. 2012). TREECS™ has been applied and validated substantially over its development (Dortch et al. 2011b, Dortch 2012, Dortch 2013, Dortch et al. 2013a, Johnson and Dortch 2014b, and Dortch 2016).

A source loading model provides the source mass loading rate within an area of interest (AOI). There are three options within the AOI loading model: 1) estimate MC residue loadings within an impact area stemming from munitions items fired on range; 2) estimate MC loadings at range firing points; and 3) specify generic source loading that could represent any other scenario not pertaining to firing ranges. The latter option is simply a table of loading rates per year (grams/year) for each constituent of concern; thus, this option could be used for applications that do not pertain to firing/training ranges. For each munitions item used on a range, the user first selects the munitions identification using the munitions type and the Department of Defense Identification Code (DODIC) or National Stock Number (NSN). The amount of MC mass in each munitions item must be known to compute the MC residue loading. This information can be obtained from the Munition Items Disposition Action System (MIDAS)[6] based on DODIC or NSN. However, extraction of information from MIDAS can be slow and tedious. A utility was developed for automatically pulling this information into the TREECS™ application. The munitions MC mass is distinguished between that used at firing points and that used at impact areas. For each munitions item fired into the impact area, the user provides the following for each year of input: number fired; percent of duds (no explosion); percent of low order detonations (partially exploded); percent yield (portion of MC used up when munitions explode) for low order detonations; percent of duds that are sympathetically exploded by another detonation; percent yield for sympathetic detonations; and percent yield for high order detonations.

[5] http://mepas.pnnl.gov/FramesV1/index.stm

[6] https://midas.dac.army.mil/

Guidance is provided within TREECS™ for estimating dud rates, low order rate and yields, and high order yields. Little information is available to date for sympathetic detonations. For firing points, the user must enter for each item fired either the emission factor, which is the mass of unused MC deposited per item, or the percent of unexpended firing point MC for each item fired. The user must also enter the numbers fired each year for each item. The other inputs that are required for impact areas are not required for firing points. Once the MC mass delivered to the impact area or firing point is known for each munitions item used and the other input parameters are entered, the calculation of residue mass loadings becomes a straightforward summation.

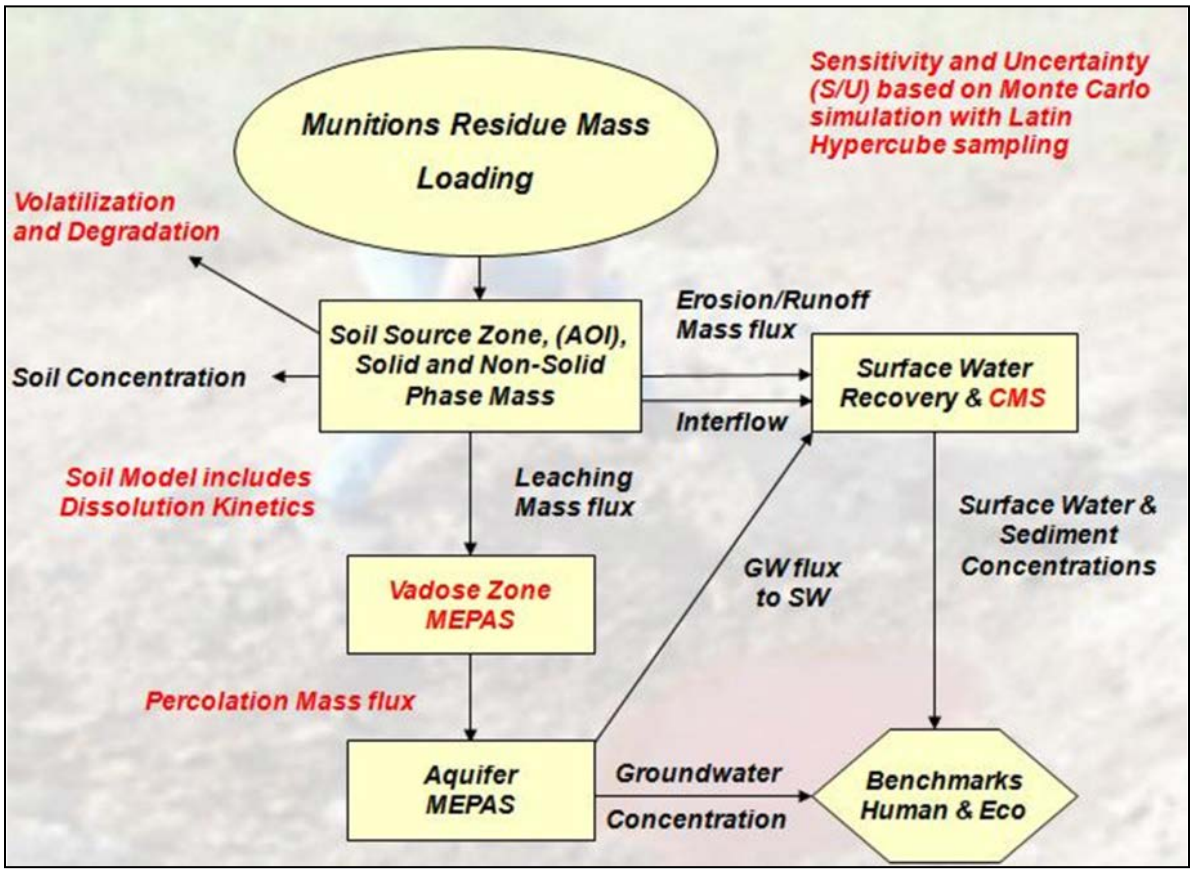

Figure 1. Conceptual Site Model and Schematic of Model Linkages within TREECS™, Tier 2.

Red denotes features in Tier 2 that are not in Tier 1

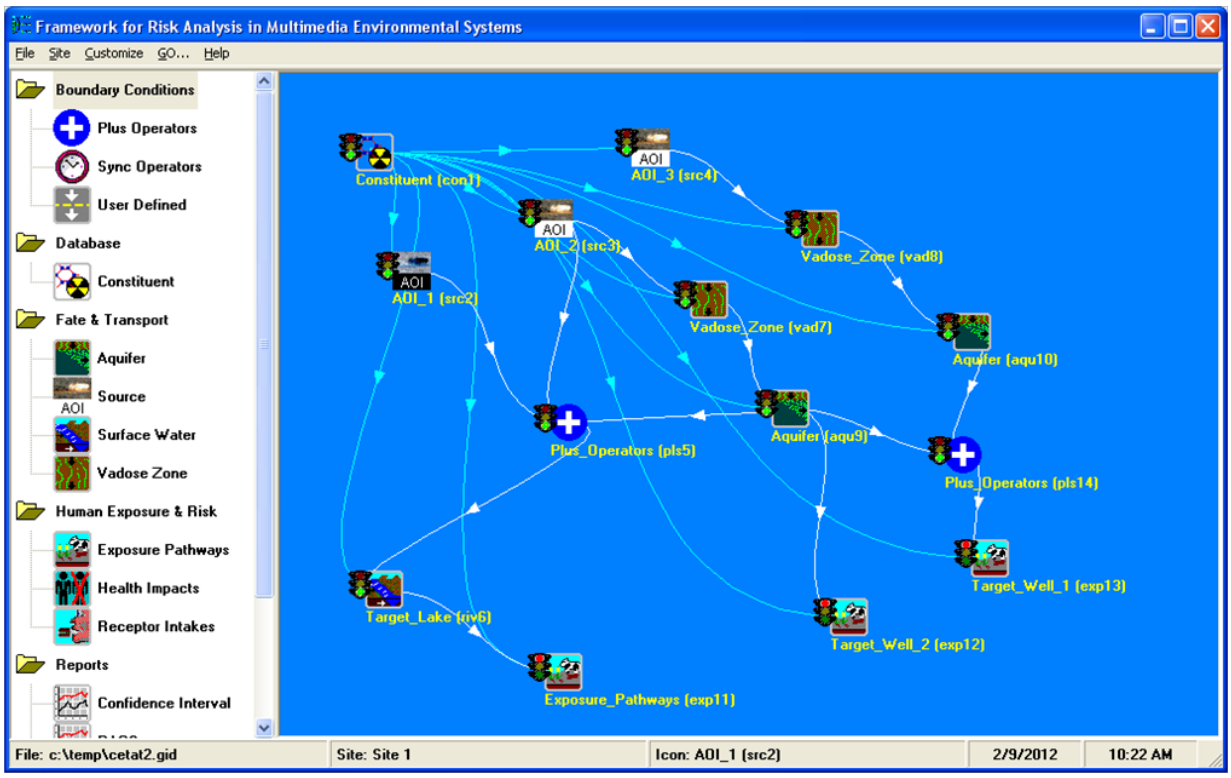

Figure 2. FRAMES CSM Workspace within TREECS™ Advanced Tier 2 Option.

All of the multimedia fate models are based on mechanistic mass balance principles. The soil model simulates a layer of surface soil that has a constituent concentration that varies with time but is fully mixed over a given AOI, such as the impact area of a live fire range. The soil model accounts for MC transport and transformations due to rain-induced erosion, surface runoff, leaching, degradation, and volatilization processes. The constituent can exist in solid and non-solid (dissolved) phases. A dissolution process is included to transfer solid-phase MC to the non-solid phases. The non-solid phase mass exists in equilibrium distributed as dissolved in water within the water-filled soil pore spaces, as adsorbed from water to soil particles, and as a vapor in air within the air-filled pore spaces. The soil model computes time-varying soil concentrations and mass export fluxes for erosion, rainfall extracted runoff, and infiltration to the vadose zone.

The fate processes in the soil model are presently driven by either average annual or daily hydrology (i.e., precipitation, runoff, infiltration, and erosion) and the user selects which option to use. There is a TREECS™ utility, referred to as the Hydro-Geo-Characteristics Toolkit (HGCT) to estimate average annual and daily hydrologic inputs. Formulations and methods used for estimating average annual and daily hydrology are described by Johnson and Dortch (2014a) and Dortch (2014).

The vadose zone model uses the infiltration, or leached mass influx rate, from the soil model to compute the time-varying mass flux moving through the vadose zone and entering groundwater. The vadose and groundwater, or aquifer, models are legacy models originally used within the Multimedia Environmental Pollutant Assessment System (MEPAS) (Buck et al. 1995).

The MEPAS version 5.0 models[7] compute fluxes through the vadose zone and aquifer, and resulting aquifer concentrations, at specified well locations. The vadose zone model solves the vertically one-dimensional (1D), reactive transport equation for partially saturated conditions. The aquifer model solves the reactive transport equation for 1D, longitudinal advection, and three-dimensional (3D) dispersion for saturated conditions. First-order degradation and reversible, linear equilibrium partitioning are used in both models. The scientific documentation of the MEPAS groundwater models is provided by Whelan et al. (1996) and Dortch et al. (2011a).

There are two options for modeling contaminant fate in surface water and sediments: RECOVERY (Ruiz and Gerald 2001) and the Contaminant Model for Streams, or CMS (Fant and Dortch 2007). Both models are legacy ERDC models. RECOVERY is best suited for pooled surface water, such as ponds and lakes, while CMS is best suited for streams and rivers. Descriptions of these two models are provided by Dortch et al. (2011a). Both models solve time-varying mass balance equations for total (dissolved and particulate) contaminant mass in surface water and bottom sediments with reversible linear equilibrium partitioning between dissolved and adsorbed particulate forms. First-order degradation kinetics are used in both models. For the RECOVERY model, the water column is treated as a fully mixed single compartment. The bottom sediments are layered into two types: a single, mixed sediment layer at the sediment-water interface; and multiple, 1-cm-thick, deep sediment layers below the mixed layer. This treatment results in three mass balance equations with three unknown variables, which apply to the water column, the mixed sediment layer, and the deep sediment layers. Two coupled ordinary differential equations are solved for the surface water and the mixed sediment layer. A partial differential equation is solved for the deep sediment layers. Fate processes include water column flushing; sorption partitioning in the water column and benthic sediments; degradation in water and sediments; volatilization from water; water column sediment settling and bottom sediment resuspension; deep sediment burial; mass transfer of dissolved constituent between the water column and mixed sediment layer pore water; bioturbation between the mixed sediment layer and top layers of the deep sediments; and pore-water diffusion within the deep sediments. Loading boundary conditions include inflowing contaminant mass due to export from the soil model, which includes rainfall extraction and runoff, erosion, and soil interflow fluxes. There is also an option to enter user-specified constant external loadings. The model produces output for total and dissolved concentrations in the water column and sediment bed.

The CMS is very similar to RECOVERY, with the primary difference being the dimensionality and its orientation. CMS divides the stream into 1D longitudinal (streamwise direction) segments. A single, fully-mixed compartment is used to represent the benthic sediments underneath each 1D stream water segment. There is exchange between the sediment compartment and the overlying water, just as in RECOVERY, but there is no longitudinal exchange between benthic sediment compartments except that associated with surface water fate and transport. The model solves a partial differential equation for the 1D, advection-diffusion-reaction (mass balance) equation of the surface water cells and an ordinary differential equation for each benthic sediment compartment. The CMS assumes steady, uniform flow. Stream flow can vary over time, but there is no hydraulic or hydrologic flow routing involved. There are various options for estimating the flow cross-sectional area and depth based on flow rate. The modeled fate processes are the same as those in RECOVERY except that bioturbation is not included since there is only one benthic layer.

[7] http://mepas.pnl.gov/mepas/maqu/index.html

The fate models within TREECS™ are also available within the Adaptive Risk Assessment Modeling System (ARAMS™)[8], which was developed prior to TREECS™ for the Army by ERDC under the Environmental Quality Technology (EQT) research program. The compatibility of TREECS™ models within ARAMS is possible due to the fact that the two systems use FRAMES as the underlying model linkage, operation, execution framework. Thus, as new models are developed for TREECS™, they can be wrapped in a manner so that they can be operational in both TREECS™ and ARAMS™. Likewise, models/modules within ARAMS™ can be shared within TREECS™. ARAMS™ provides the capability to conduct comprehensive human and ecological health risk assessment associated with multimedia exposure to contaminants. The human health risk models (i.e., exposure, intake, and health impacts) within ARAMS™ were added to TREECS™ and can be used by selecting the Advanced Tier 2 Modeling option within TREECS™. The ecological risk models/modules/databases of ARAMS™ have not been added to TREECS™ due to the greater complexity associated with these items. Range applications of TREECS™ typically will not require a comprehensive human or ecological health risk assessment, and the screening level assessment that is readily available and easily used within TREECS™ will be sufficient, especially given the fact that the screening level protective heath benchmarks are highly conservative.

If a more comprehensive ecological health risk assessment is required for a range application, then there are two options for doing this. These two options also apply to conducting a comprehensive human health risk assessment, in addition to the third option made available by applying TREECS™ Advanced Tier 2, as described above. One option is to apply ARAMS™ using TREECS™ fate models within ARAMS™. The other option is to apply TREECS™ and then supply the TREECS™-predicted media concentrations to ARAMS™ by using the *User Defined* modules within ARAMS™ that allow use of known concentrations within media. The latter option is preferred since TREECS™ has many other features (tools and information) to facilitate range applications that are not available within ARAMS™. Additionally, the time required to learn to use TREECS™ Tier 2 is much less than that of ARAMS™ due to the more structured development approach of TREECS™. All risk characterizations within the scope of this project will be screening level and will be based on the conservative protective health benchmarks available within TREECS™. The benchmarks are within the TREECS™ DoD Health Benchmarks Database and were provided by the DoD Range Munitions Use Subcommittee (RMUS).

The CTS Environmental Systems Modules and Workflows are illustrated in Figure 3. Figure 4 provides an illustration of the front page of CTS that provides the user with options for the selection of the CTS workflows and descriptions of the CTS modules, physicochemical property calculators, and reaction libraries. When executing a CTS workflow, the user enters the system through the Chemical Editor (Figure 5), which allows for entry of the chemical of interest through either provision of the common name, smiles string notation, CAS registry number, or chemical structure. The user then defines the environmental conditions of interest (e.g., aerobic versus anaerobic). Based on the environmental conditions selected by the user, the Reaction Pathway Simulator (Figure 6) will provide the major transformation products based on the execution of reaction libraries for abiotic reduction, hydrolysis, and/or aerobic biotransformation. The parent chemical and the generated transformation products are then passed to the Physicochemical Properties Calculator (Figure 7),

[8] http://www.erdc.usace.army.mil/Media/FactSheets/FactSheetArticleView/tabid/9254/Article/500113/adaptive-risk-assessment-modeling-system-arams.aspx

which through access to SPARC (SPARC Performs Automated Reasoning in Chemistry) (Hilal, 2003), EPI Suite (Boethling and Constanza, 2010), TEST (Martin, 2016), and ChemAxon's plug-in calculators, will provide the necessary physicochemical properties required for predicting environmental concentrations. The fully functional version of the CTS will include a Reaction Rate Calculator that will provide reaction rate constants based on the parameterization and execution of available quantitative structure-activity relationships (QSARs). In this version of the CTS, the user will also have the ability to generate environmental descriptors through execution of the Earth Systems Module. This module uses Data for Environmental Modeling (D4EM) to search online databases (e.g., the United States Geological Survey (USGS) Water Quality Database) for environmental descriptors, such as groundwater temperature, organic carbon content, and pH.

The most recent version of TREECS™ available to the public is version 5, which was released October 2013. There is another developmental version that has not been released to the public which contains BMP modules. The newer version will be released in early 2017. The CTS is a web-based tool that is currently running on cloud-based servers behind the EPA's firewall. The most recent version of CTS will made available to the public in early 2017. The prototype CTS was used during 2014 to expand the Army Range Munitions Constituents Database (ARCDB) to include additional physicochemical properties (e.g., ionization constants), as well as the degradation products (including their physicochemical properties) resulting from reductive transformations.

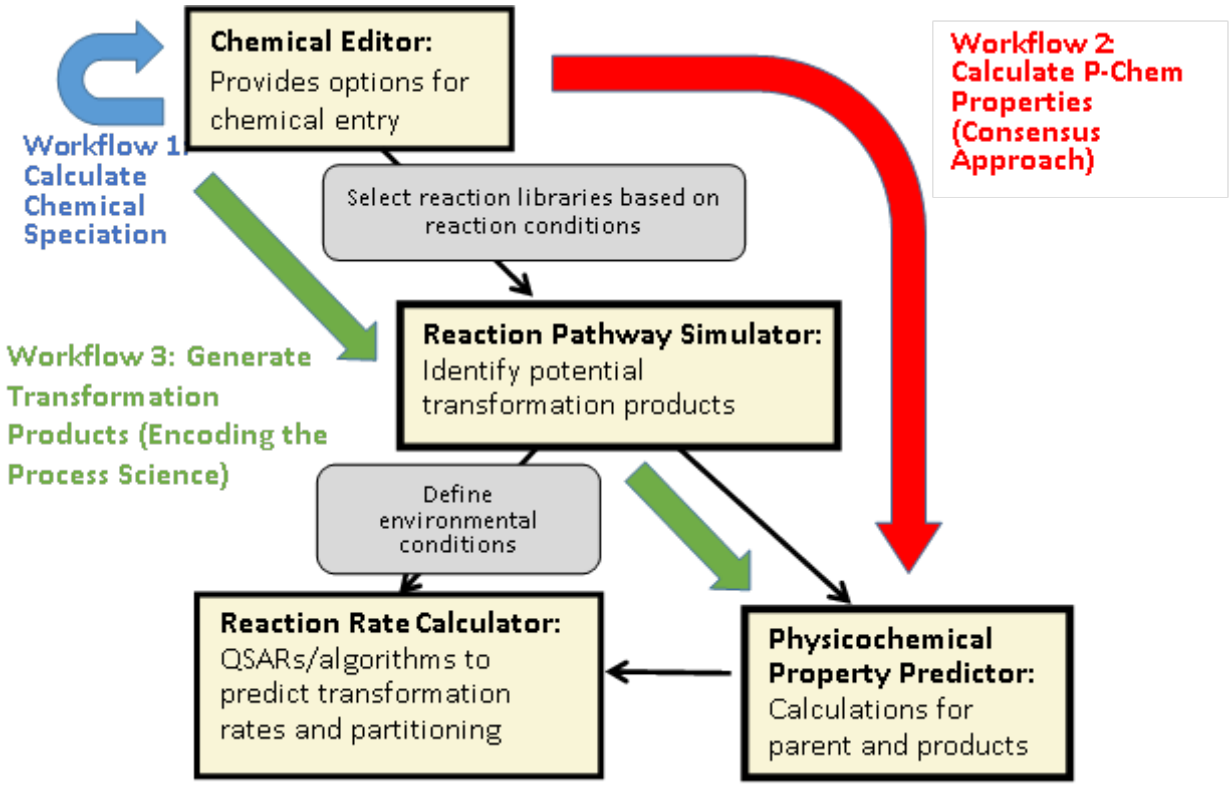

Figure 3. The Primary Modules and Work Flow Diagram for CTS.

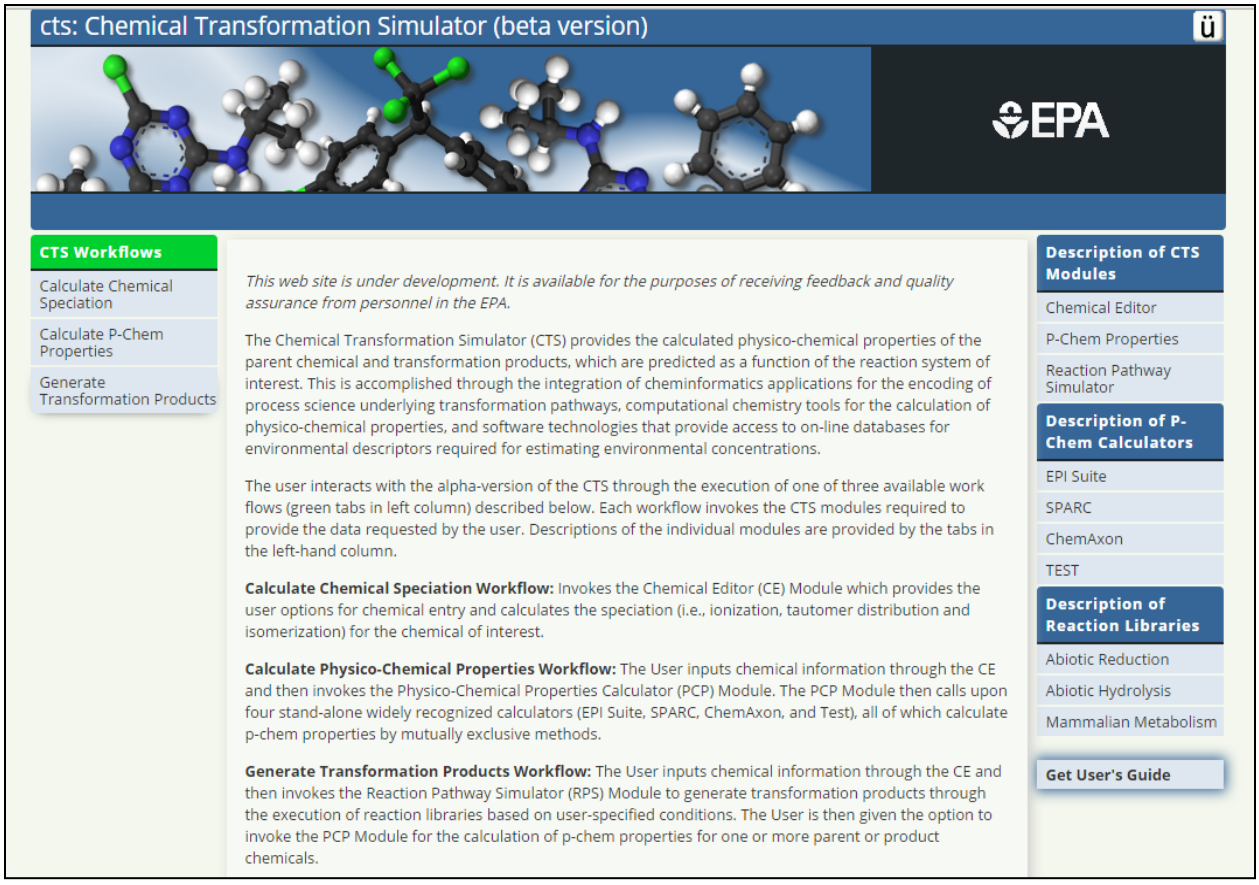

Figure 4. Front Page of CTS Providing the User with Options for the Selection of the CTS Workflows and Descriptions of the CTS Modules, Physicochemical Property Calculators, and Reaction Libraries.

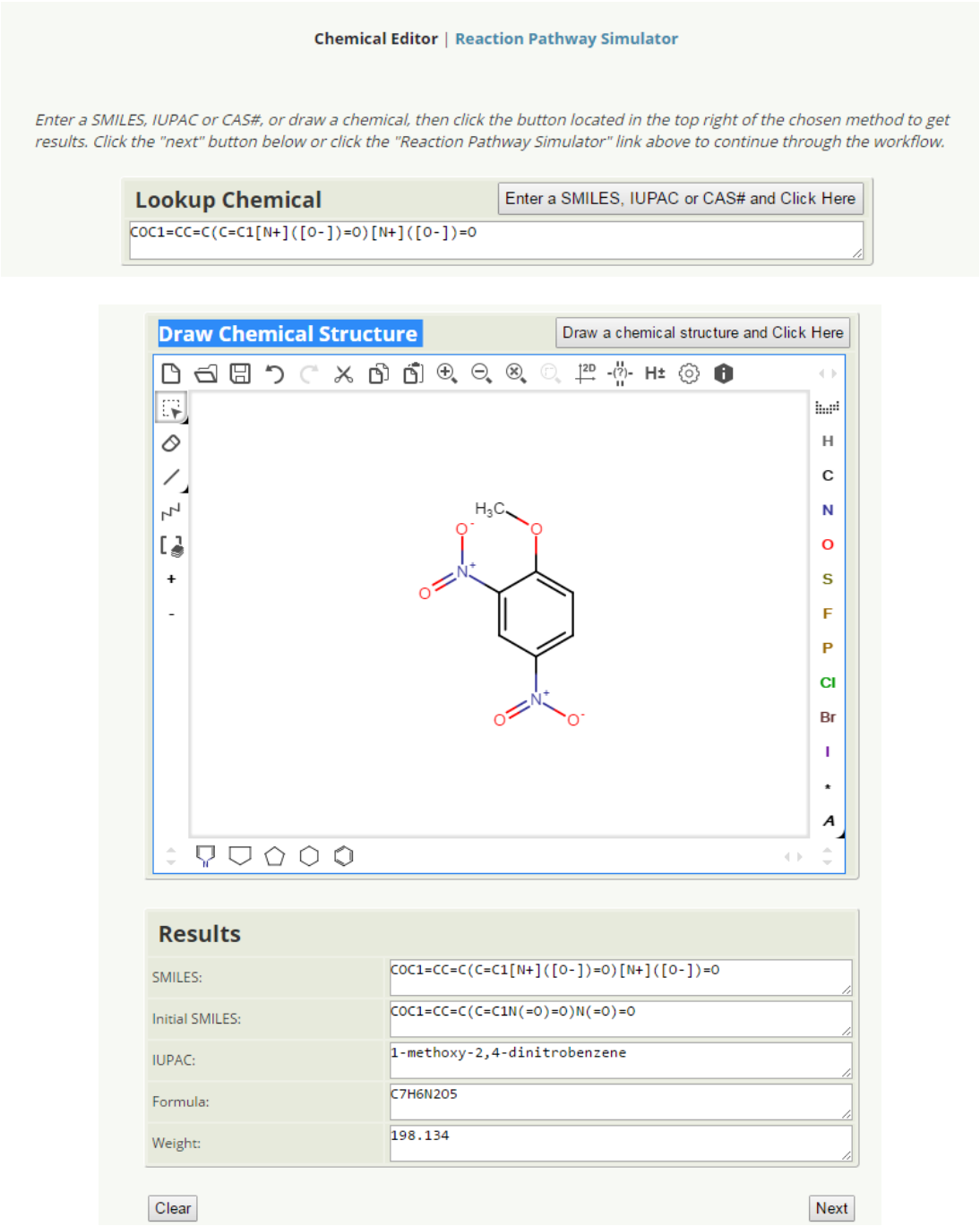

Figure 5. CTS Chemical Editor Module

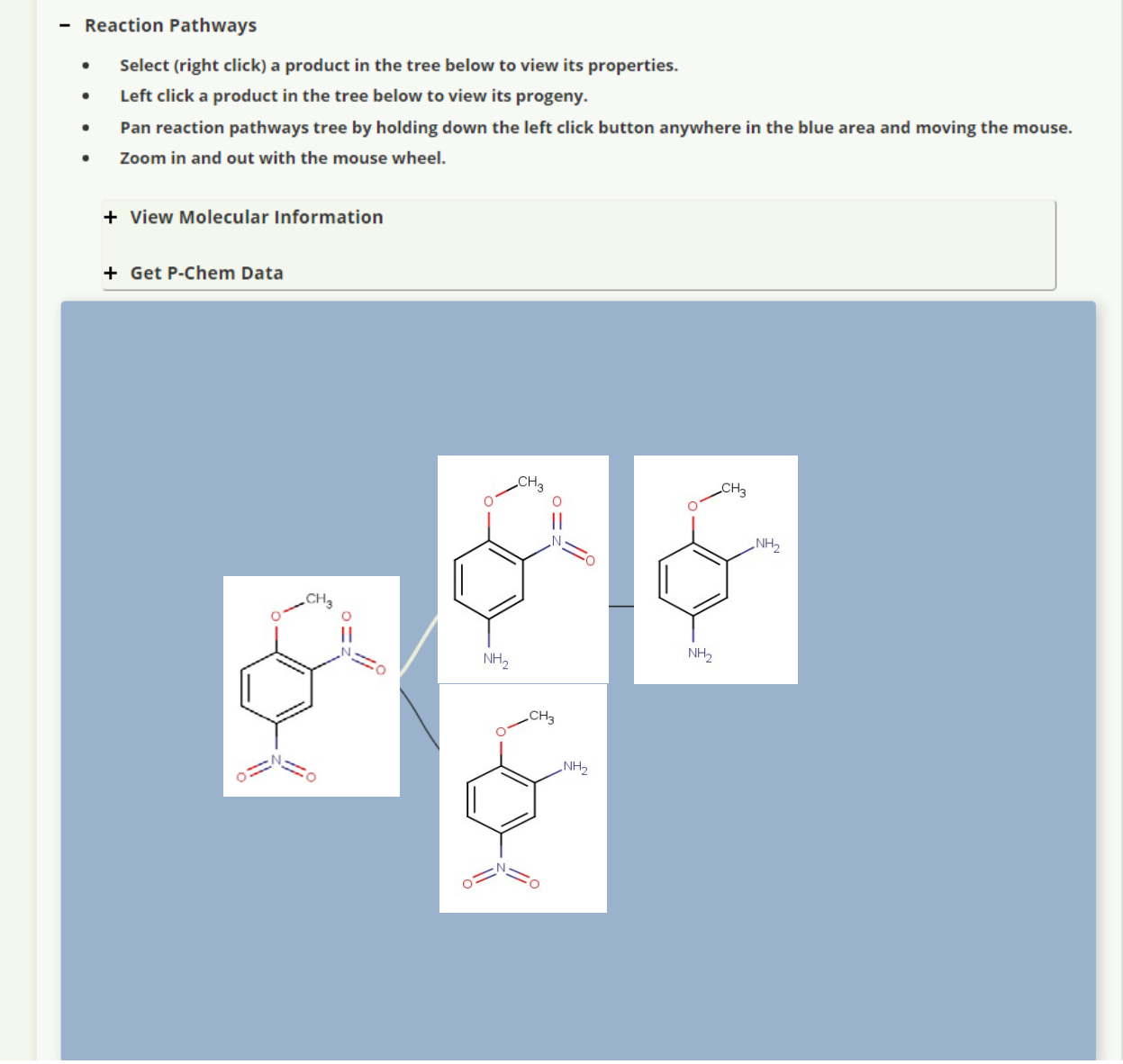

Figure 6. CTS Reaction Pathway Simulator Module.

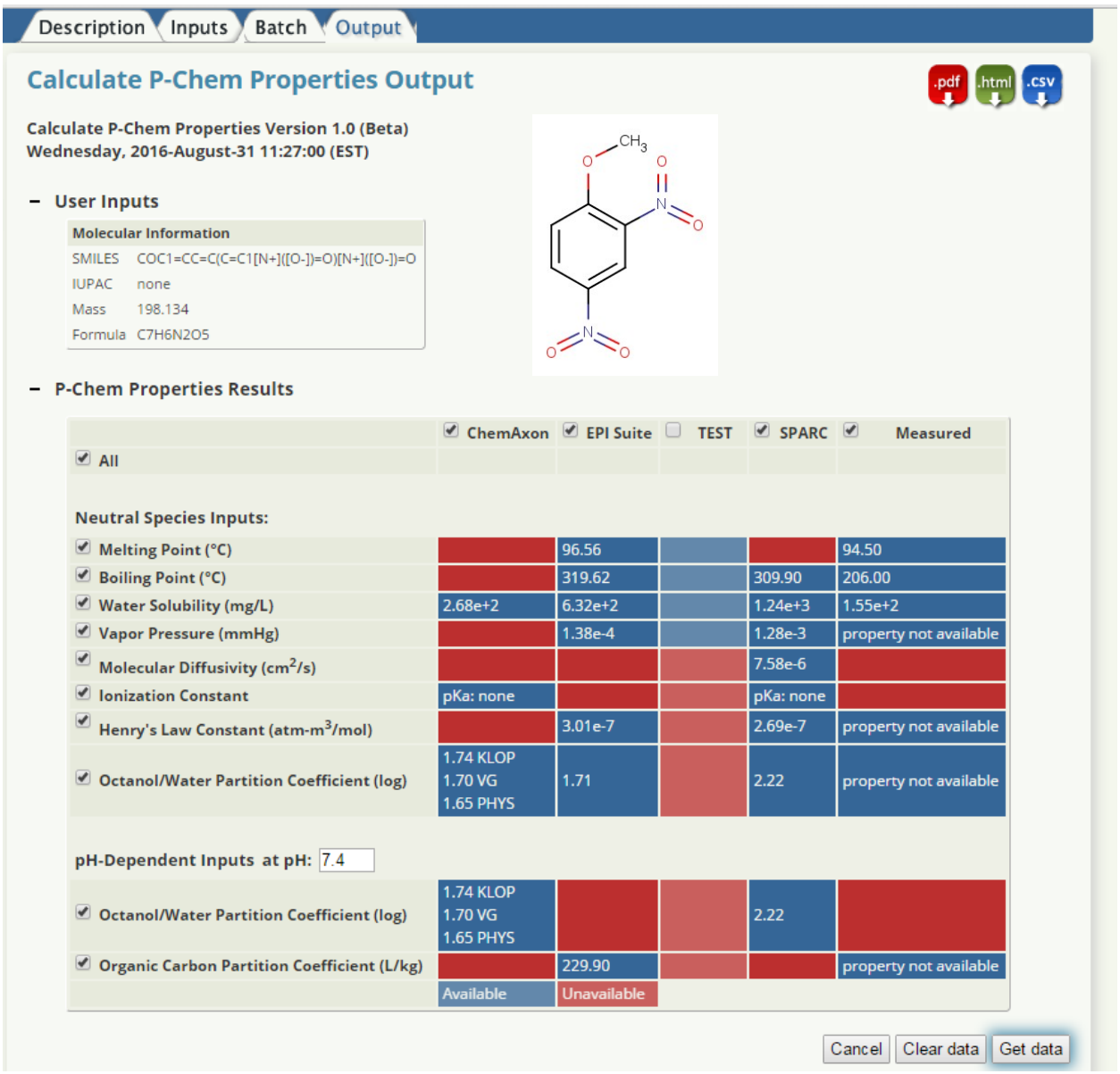

Figure 7. Example Output from the CTS Physicochemical Properties Calculator Module.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The primary advantage of TREECS™ is that it provides a single, standardized suite of tools for specifically assessing military training and firing range operations and management to provide long-term viability to meet the national defense mission while protecting the environment and human health. Although the Marine Corps has used a variety of public domain contaminant fate models in their REVA process, none of these models are customized specifically to address range environmental issues like TREECS™. Thus, TREECS is unique from this application standpoint. However, TREECS™ is still general enough that it can be used for non-military applications.

Advantages of TREECS™ are highlighted via the following unique, TREECS™-specific features:

- Tiered analysis to allow staged assessments from initial screening to more comprehensive.
- Geographic Information Systems (GIS) module to facilitate applications with linkage to HGCT for estimating model inputs.
- Range munitions residue loading estimation module.
- Internal munitions data base indexed by DODIC and/or NSN based on a sub-set extraction from MIDAS for providing MC mass within each type of munitions.
- Three databases for providing constituent physicochemical properties, including the ARCDB, which is tailored to range-specific contaminants.
- DoD RMUS ecological and human protective health benchmarks database.
- Automated linkages among multimedia contaminant fate models to facilitate ease-of-use for assessing source-to-receptor exposure.
- Special internal tools for estimating fate process input parameters, such as HGCT and soil-water and sediment-water adsorption partitioning coefficients.
- Sensitivity and uncertainty analysis via use of the built-in Monte Carlo simulation module.
- Specialized viewers to facilitate rapid examination and presentation of results.
- Reference indexing and tracking system and input summary report to document sources and values of input data.
- Database editors to allow development of user-specific databases for constituent properties, protective health benchmarks, and munitions component masses.
- Graphical user interfaces (GUIs) on all models to facilitate model set-up.
- BMP assessment modules.

Given the above features, TREECS™ can be applied in a relatively short period of time to determine range vulnerability for release of MC of concern from an operational range to an off-range area. Furthermore, TREECS™ can be used to determine when such a threat could occur, thus providing the capability to evaluate future potential threats for existing or proposed ranges. For ranges that pose a threat for MC exposure in off-range areas, it can be used to evaluate alternatives to reduce or negate that exposure. The primary limitation of TREECS™ is that it does require a level of understanding relative to environmental modeling, which is true for applying any type of model. However, many features have been provided to try to minimize the time required for a user to become proficient. TREECS™ utilizes models of reduced form to minimize input requirements and the level of model complexity. Limiting the number of spatial dimensions and/or assuming property uniformity are a means of reducing model form. Models of reduced form can provide insightful information rapidly with first-order accuracy; however, the primary limitation of such models is that they may not be able to capture the effects of complex site features, and in such cases, a more comprehensive model may be required.

CTS is a unique product providing a wide range of physicochemical properties for organic contaminants and for their predicted transformation products. This capability is of interest for emerging contaminants especially, which have lesser-known properties. The limitations of CTS are that it is not applicable to metals and it does not predict degradation rates for organic chemicals.

3.0 PERFORMANCE OBJECTIVES

The demonstration performance objectives and success criteria for this project are shown in Table 1. It is noted that each performance objective is evaluated for each study site except for the second qualitative objective (training), which is independent of study sites.

Table 1. Demonstration Performance Objectives and Success Criteria.

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives[9]		
TREECS™ accurately simulates long-term fate of MC on ranges	• Receiving water MC concentrations • Information to estimate historical firing rates of munitions on range, such as firing records • Various site characteristics required for modeling MC fate	• Highly successful: model concentrations within a factor of 3 of observed • Successful: model concentrations within a factor of 5 of observed • Unsuccessful: model concentrations greater than a factor of 5 of observed
TREECS™-CTS can be used to quantify uncertainty in inputs	• Receiving water MC concentrations • Information to estimate historical firing rates of munitions on range, such as firing records • Various site characteristics required for modeling MC fate	• Model sensitivity and uncertainty feature can be used to bracket observed field MC concentrations at the 95% confidence level
Qualitative Performance Objectives		
TREECS™-CTS can be quickly set up and run with readily available data	• Information to estimate historical firing rates of munitions on range, such as firing records • Various site characteristics required for modeling MC fate	• TREECS™, including CTS use, can be set up for a site within 80 labor hours using readily available information
Training requirements are reasonable	• Installation personnel or contractors that are available and willing to participate in TREECS™-CTS training and will apply the system • Interviews with personnel and contractors following system training and use	• Engineer or scientist with general background in modeling, hydrology, and water quality can be trained to use system in 3 days to apply the system
TREECS™-CTS can be applied to evaluate range management and/or remediation strategies	• Data noted above to accomplish model setup and validation • Future uses of range • Information pertaining to the specific management or remediation alternative to be addressed	• TREECS™-CTS can be used to evaluate three management and/or remediation strategies to reduce MC concentrations in target receiving water
TREECS™-CTS can be applied to evaluate the fate of emerging MC	• Input data files for previous application sites • Physicochemical properties of emerging MC to be evaluated	• TREECS™-CTS can be used to evaluate the fate of four emerging contaminants that are used in new insensitive munitions (IM) by comparing results to those of conventional MC, such as RDX

The last qualitative performance objective was added after the original work plan development. This objective will demonstrate the capability of TREECS™-CTS to evaluate the fate of MC for

[9] Observed data are too limited to do anything more robust for comparison, such as various statistical metrics.

new IM formulations relative to conventional MC, such as RDX. Five emerging contaminants (EC), 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), ammonium perchlorate (AP), and hexanitrohexaazaiso-wurtzitane (HNIW), also known as CL-20, will be tested and fate results will be compared against Royal Demolition Explosive (RDX) for three study sites. This demonstration will show the powerful utility of the modeling system for evaluating the fate and exposure of EC in the environment.

4.0 SITE DESCRIPTION

The approach called for applying the TREECS™/CTS systems to three DoD sites where receiving water concentrations of MC have been measured, thus allowing demonstration and validation of the models against observed data. Three sites were selected for study, as detailed in the Site Selection Memo for this project. The three study sites are: Demolition (Demo) Area 2 of Camp Edwards of Massachusetts Military Reservation (MMR), MA.; the Artillery Impact Area (AIA) of the U.S. Military Academy (USMA), West Point, NY.; and Zulu Impact Area (ZIA) of Marine Corps Base (MCB) Camp Pendleton, CA. The MC of interest at all three sites is the HE hexahydro-1,3,5-trinitro-1,3,5-triazine, referred to as RDX. Groundwater was modeled for Demo Area 2 of MMR. Surface water (Popolopen Brook) was modeled down-gradient of the AIA at West Point. Surface water and groundwater were modeled for the Las Flores watershed that contains the ZIA. Demo Area 2 is the only site that has more than two observed receiving water concentrations of RDX, but all three sites do have observed values exceeding detection limits, which is often not the case at many installations where either sampling has not been performed for receiving waters or receiving water samples are below detection for various reasons (e.g., limited transport to sampling location or poorly conceived sampling locations and/or sampling times). All three sites were useful for investigative modeling of ECs associated with new IMs with comparison to RDX.

Since there are three study sites, the format of this report must depart some from the ESTCP guidance, in which it is assumed that there is one study site. In the final report for this project (Dortch et al. 2017), there are three separate major sections devoted to each study site application. Each of those three major sections includes the description of the study site. Additionally, this project involved modeling, rather than field sampling and demonstration of a site remediation technology. This aspect further required departing from the ESTCP report format. For these reasons, the ESTCP guidelines for sections 4 and 5 could not be followed here and for the final report. For the final report, the information required by the ESTCP guidelines was captured within each of three major sections that dealt with each study site application. For this cost and performance report, only the first application study (MMR Demo Area 2) is presented for the sake of brevity while providing a sample of what is fully contained within the final report (Dortch et al. 2017). The final report should be accessed for results of the other two study sites. Section 7 herein on Performance Assessment provides a brief summary of results for the other two study sites.

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5.0 TEST DESIGN

This section provides the detailed description of the system design and testing conducted during this demonstration project. As explained in the previous section, it is impossible to follow the ESTCP final report and cost/performance report format since this project is vastly different from the typical ESTCP Environmental Restoration project that involves field sampling and demonstration of a restoration technology. The sub-sections that follow are closely tied to the performance objectives of Table 1.

5.1 OVERALL CONCEPT

Accomplishment of the first quantitative performance objective dealing with model validation is the key to successful accomplishment of the other objectives, with the exception of the first qualitative performance objective associated with model set up. There is an important aspect of validation in this study that is common to all three study sites. Model inputs were set initially based on the best available information, without regard to how well model results compared with observed data. In other words, input data were not manipulated to force the model to agree exactly with the observed data. Adjustments were made to any inputs that were determined to be inappropriate or were discarded due to improved information or understanding of the modeled system. However, there was no attempt to force calibrate each site model to agree with measured results. Thus, model *calibration* was not performed, and any model input adjustments herein should not be interpreted as calibration (e.g., adjustment of an instrument for taking measurements). TREECS™ was developed to predict or forecast MC fate and concentrations in the environment based on past and future range operations. It is impossible to calibrate the models for such predictions. For this reason, it is far more important to validate the use of TREECS™ for predictive use than to force calibrate it to exactly match past observations. Thus, there is no forced model calibration, rather, the focus is on model validation using the best available and reasonable information for model inputs.

5.2 MODEL VALIDATION

The accuracy of each validation was quantified to the extent possible, which depends on the amount of available field-measured data. A set of metrics were needed for evaluating model validation success. Due to the scarcity of observed MC concentration data, statistical comparisons were not possible in most cases; thus, model results are compared to observed data in two other ways, result ratio (*RR*) and relative error (*RE*). The *RR* is the ratio of model-predicted (*P*) to observed (*O*), or the inverse, as follows:

$$RR = \frac{P}{O}, if\ P \geq O \quad or \quad RR = \frac{O}{P}, if\ P < O \tag{1}$$

The *RR* provides the factor by which the model either over- or under-predicts the observed value, and it is always greater than 1.0 unless the prediction is perfect, in which case *RR* = 1. The *RE* is a percent of error computed from:

$$RE = 100\,\frac{|P - O|}{O} \tag{2}$$

The *RR* and *RE* are related, but relating them can be somewhat misleading. For example, consider two model results that over-predict and under-predict by a factor of 2 (i.e., *RR* = 2). For the over-prediction, *RE* = 100%, but for the under-prediction, *RE* = 50%. Similarly, consider two model results that over-predict and under-predict by a factor of 3 (i.e., *RR* = 3). For the over-prediction, *RE* = 200%, but for the under-prediction, *RE* = 66.7%. An *RE* of 50% (or 66.7%) appears to be a lot better than an *RE* of 100% (or 200%), but in reality, the model disagreement with observation is the same but only over-predicted in one case and under-predicted in the other. Thus, the *RR* was used to determine whether or not the performance objective has been met, where the criteria for highly successful for the first quantitative objective is *RR* = 3. However, *RE* was also reported to document the amount of model error relative to the observation.

5.3 BASELINE CHARACTERIZATION

The final validated model for each of the three study sites served as the baseline condition for sensitivity and uncertainty analyses. The final validated model was also used for the baseline conditions for demonstration and evaluation of range management and BMP alternatives. The media concentrations for each management alternative are compared with no-action baseline concentrations. In the absence of future range use plans, recent range usage (i.e., munitions firing rates or MC loading rates) was assumed for future years to establish future no-action baseline conditions. All other inputs were the same as the final validated model. The alternative action conditions, which include input modifications for each alternative management strategy, were run and compared against the no-action baseline condition. Similarly, baseline conditions were used to assess the fate of each of the ECs for each study site relative to that of RDX.

5.4 FIELD DATA

Field sampling and testing were not conducted during this project, rather, existing field data were used for assessing the accuracy of model-computed results. Model output for the appropriate media and location, year, and concentration units compared with observed data for that media, location, time, and units. The comparisons that are made are summarized in Table 2.

Table 2. Available Observed Data for Model Comparison.

Study Site	Media	Year	Type of observation concentration for RDX
Demo Area 2, MMR	AOI[1] soil	1998	Total
Demo Area 2, MMR	Groundwater	2001 - 2015	Dissolved
AIA, USMA	Surface water creek	2003	Total
AIA, USMA	Surface water creek	2012	Total
Zulu impact area, Camp Pendleton	Surface water creek	2011	Total
Zulu impact area, Camp Pendleton	Groundwater	2012	Dissolved

[1] AOI = area of interest, such as in impact area of firing ranges

5.5 UNCERTAINTY ANALYSIS

Following model validation, the uncertainty analysis capability of TREECS™ was demonstrated for the MC of interest at each study site. TREECS™ uses Monte Carlo simulation with Latin Hypercube sampling for assessing uncertainty in model inputs. The inputs treated as uncertain were selected based on sensitivity testing. The performance objectives called for delineating the 95% confidence band for predictions and determining if the observed data fall within that band.

5.6 FATE OF EMERGING MC (EC) ASSOCIATED WITH IM

The third component of each study site application involved applying the systems for emerging contaminants or constituents (ECs), which include components of newer IM. The applications for ECs are provided to demonstrate the utility of TREECS™ - CTS for forecasting the fate of newer MC relative to the fate of traditional MC (e.g., HE RDX). The physicochemical properties of newer MC are not as well known, and field data are non-existent.

Insensitive munitions contain explosive constituents that are less sensitive to heat and shock. Three IMs receiving attention include IMX 101, IMX 104, and PAX 21. The ingredients of IM include 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), nitroguanidine (NQ), and ammonium perchlorate (AP). RDX is included in some IMs, such as IMX 104 and PAX 21. Another new HE of interest is HNIW, also known as CL-20. The fate of these five MCs was evaluated at each study site relative to RDX.

5.7 BMP ASSESSMENT

The fourth component of each study site application involved demonstration of the capability to assess BMP alternatives, including remediation strategies, for reducing environmental risk. Three BMP alternatives were evaluated for each site using the original MC of interest (RDX) for that site.

The section that follows is devoted to the first study site, Demo Area 2 of MMR. Within that major section, there are sub-sections explaining site description, model inputs, model validation results, uncertainty analysis, fate of ECs, and BMP assessment. The final report for this project (Dortch et al. 2017) has two additional major sections similar to the next section that detail the study site application for the other two study sites. Those sections are not repeated here, but the results are summarized in the section on Performance Assessment.

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6.0 MMR DEMO AREA 2 APPLICATION

6.1 SITE DESCRIPTION

The Massachusetts Military Reservation (MMR) is located in Barnstable County in the Cape Cod region of Massachusetts. The installation has been in use since 1911 for Army training and maneuvers, military aircraft operations, maintenance, and support. There are currently units or members of the National Guard operating at the MMR.

Demo Area 2 is located in the northern section of Camp Edwards, which is within the MMR as shown in the site map of Figure 8. Demo Area 2 was used for light demolition training for roughly 10 years, (beginning in about 1978 and continuing until about 1988). The area was used for demolition training, not for demolition of loaded munitions; thus, non-munitions objects were blown up rather than munitions containing explosives. Range records show that the explosives used in this area were limited to blocks of Composition 4 (C4) and trinitrotoluene (TNT) demolition charges. Thus, C4, which contains RDX and plasticizers, was a prevalent explosive at this site. Some charges may not have experienced full, high-order detonation, thus resulting in unexploded HE residue. RDX residue from these explosives infiltrated the groundwater beneath the demolition range.

The soils in this region are sandy and highly permeable, allowing for rapid movement of groundwater at rates up to 0.6 m/day (AFCEE, 2006). The MMR is located over the recharge area of the Sagamore Lens, which is a large aquifer about 91 m thick (AFCEE, 2006). Demo Area 2 is divided into four main soil regions, but the source zone area is characterized as Enfield soil type (denoted as 265B), which is silty loam down to 30 cm, a mixture of silty loam and sandy loam from 30 to 79 cm, and mostly sand at depths below 79 cm.

Soil and groundwater concentrations of RDX were measured at the site about 10 to 15 years after demolition training had ceased. The RDX groundwater plume delineation relative to monitoring wells near Demo Area 2 is shown in Figure 9. The darker shade indicates concentrations greater than 2 parts per billion (ppb), which was the public health advisory concentration at the time, and the lighter shade indicates concentrations above non-detection but less than or equal to 2 ppb.

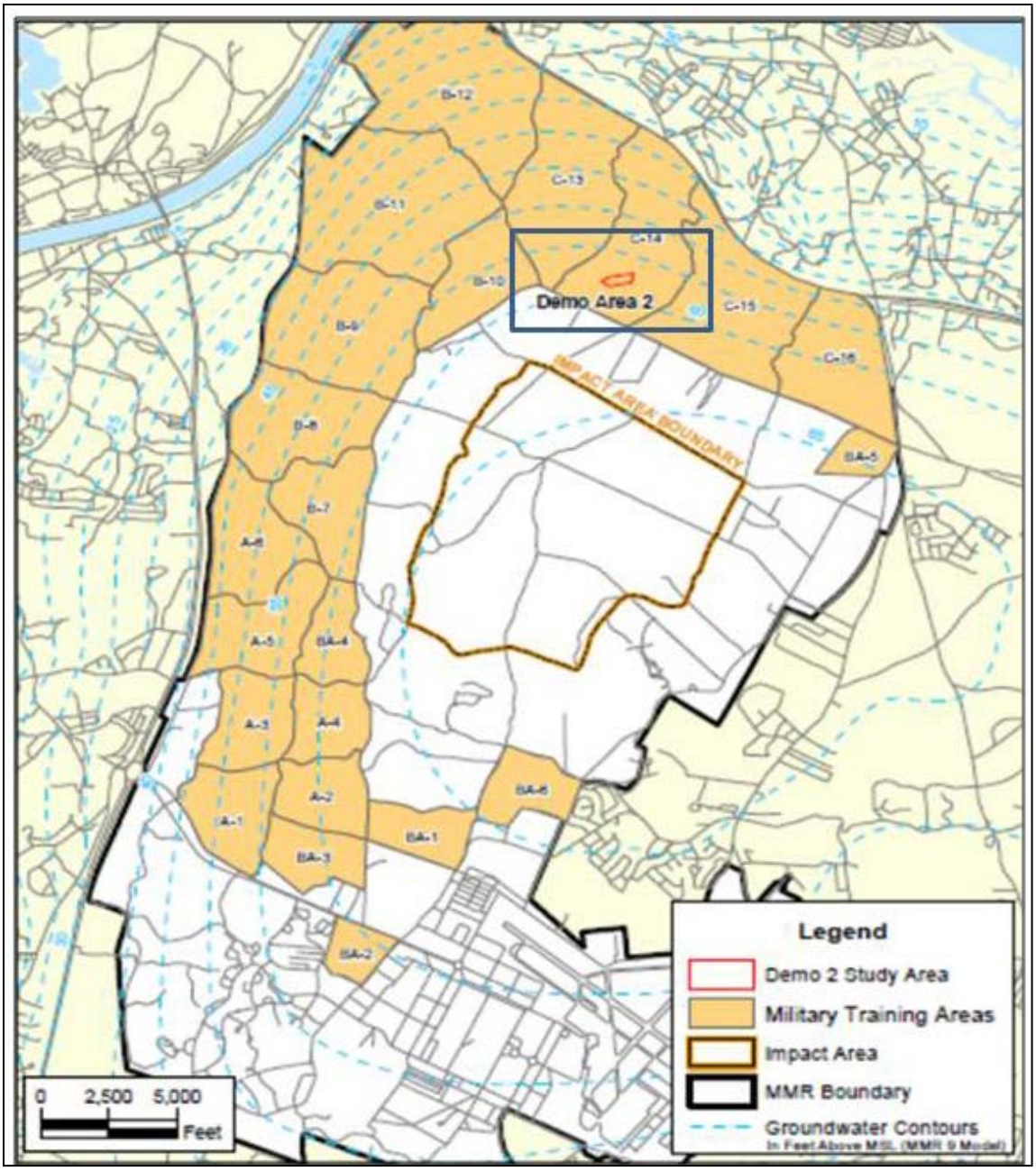

Figure 8. Demo Area 2 of MMR, Cape Cod, MA.

Modified from AMEC Earth and Environmental, 2004

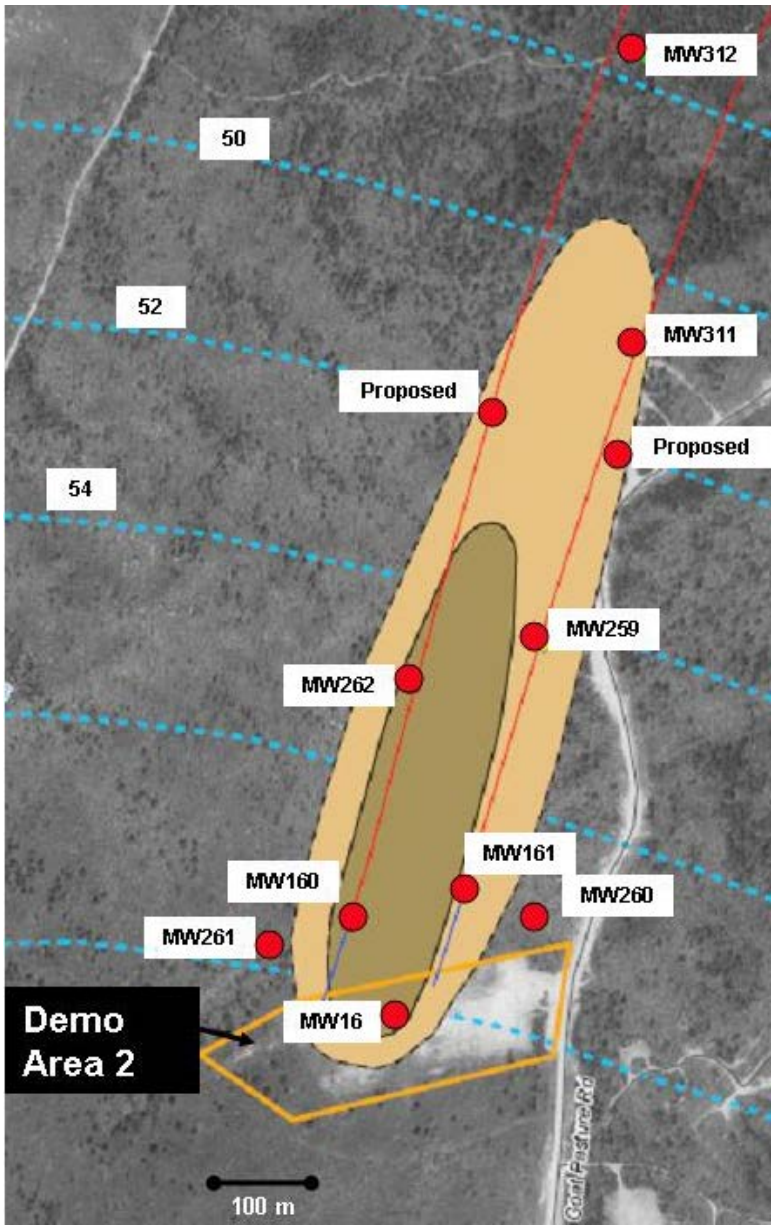

Figure 9. RDX Plume Delineation and Monitoring Wells for Demo Area 2 with Groundwater Contours in Feet National Geodetic Vertical Datum (NGVD).

Modified from AMEC Earth and Environmental, 2004

6.2 MODEL INPUTS FOR VALIDATION

Demo Area 2 and the receiving groundwater were modeled previously with TREECS™ (Dortch et al. 2007; Dortch 2012). This study site was modeled again (Dortch 2015) as part of this ESTCP project. Although most of the model inputs for the ESTCP application are the same as those documented previously (Dortch et al. 2007; Dortch 2012), a few inputs were corrected as described by Dortch (2015).

Three modeling components of TREECS™ were used, which included the Tier 2 soil model, the Multimedia Environmental Pollutant Assessment System (MEPAS) vadose zone model, and the MEPAS aquifer model. The background information for the model input values are not repeated here since this information is presented in the previously referenced publications (Dortch et al. 2007; Dortch 2012; Dortch 2015). The model input values are detailed by Dortch et al. (2017). Throughout this report, the term AOI is used to refer to the soil source zone area where MC has been deposited due to military training/firing.

Key features of the model inputs for this application are noted here. The option for average annual hydrology, rather than daily varying hydrology, was used in the soil model for this application. A constant RDX residue loading rate of 1,500 g/yr was applied for 10 years, starting in 1978. This loading rate is an estimate based on the types of detonation charges used (Dortch et al. 2007). The particles of low-order detonations are on the order of a centimeter in size (Pennington et al. 2005; Taylor et al. 2004). A particle diameter of 6,000 micrometers or 0.6 cm was used for this application.

The model was run for 30 years during validation, starting in 1978 when there was assumed to be zero soil contamination of RDX. Surface soil runoff was assumed to be zero for the highly permeable soils, thus, all precipitation resulted in evapotranspiration and infiltration into the soil layer. The half-life for degradation of dissolved phase RDX in soil, vadose zone, and groundwater was assumed to be 100 years, whereas the solid and adsorbed phase RDX was assumed to be non-degradable (a high value of 1E20 years was used for half-life). Soil properties for silty loam and sand were used for surface soil and vadose/aquifer, respectively. All chemical-specific properties of RDX were obtained from the Army Range Constituent Database (ARCDB) within TREECS™. The well location for monitoring model output coincided with the location of monitoring well 161 (MW161), which is one of the wells where RDX concentrations were measured in the field.

CTS was not used during model validation to set the chemical-specific properties for RDX since those properties are fairly well known and were available in the TREECS™ constituent databases. However, values derived from CTS were used during model sensitivity analysis and assessment of the fate of IM components as discussed later.

6.3 VALIDATION RESULTS

The model-computed results are shown in Figure 10 and Figure 11 for soil and groundwater, respectively, with comparison to the mean and range of measured concentrations. Groundwater monitoring well MW161 was selected for comparisons, although fairly good model agreement with observations was obtained at all wells (Dortch et al. 2007). Groundwater observations (e.g., measurements) of RDX extended over several years (2001–2004) in Figure 11, but they all were assumed to have been collected in one year, 2003, in order to develop the mean and range of observed concentrations. The range of observed soil concentrations of RDX are due to spatial variations in soil concentration rather than any variation over time, since all measurements were obtained in the same year, 1998.

As explained previously, there was no model calibration involved in this study. Certainly, the estimated RDX residue loading rate of 1.5 kg/yr could have decreased slightly, which would have forced the model results to agree exactly with the observed concentrations. The loading rate was an estimate based on best available information, and there is certainly error in that estimate.

However, as explained previously, the purpose is not to calibrate TREECS™ to match exactly observed data, rather to validate that it can be used to predict media concentrations given best estimates for model inputs.

The performance metrics of the validation results for soil RDX concentration are *RR* = 1.29 and *RE* = 29%, where *RR* and *RE* are defined by Equations 1 and 2, respectively. The performance values for aquifer RDX concentration at MW161 are *RR* = 1.11 and *RE* = 11%. Since *RR* is less than 3 in both cases, the first quantitative performance objective is rated as highly successful according to the performance objective criteria in the Demonstration Plan. An *RE* of 29% and 11% are considered quite good.

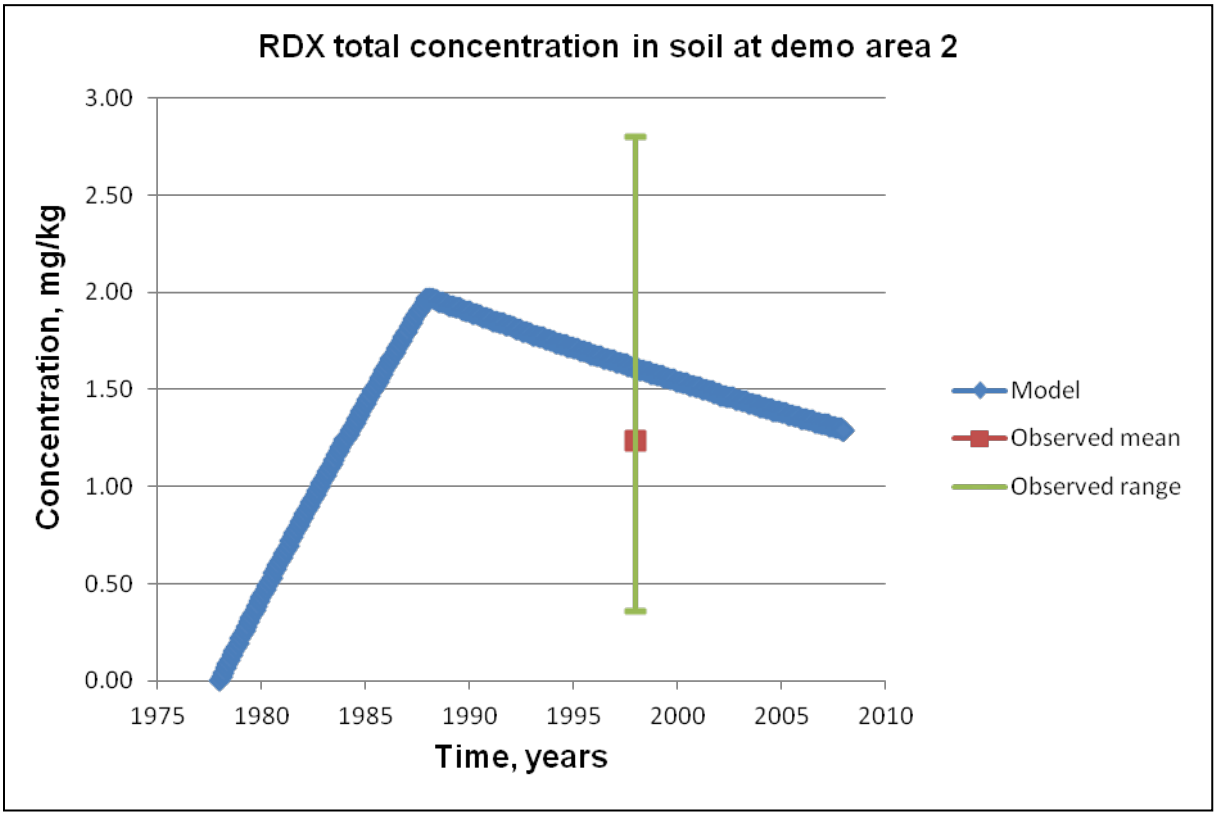

Figure 10. Computed and Observed RDX Soil Concentrations at MMR Demo Area 2.

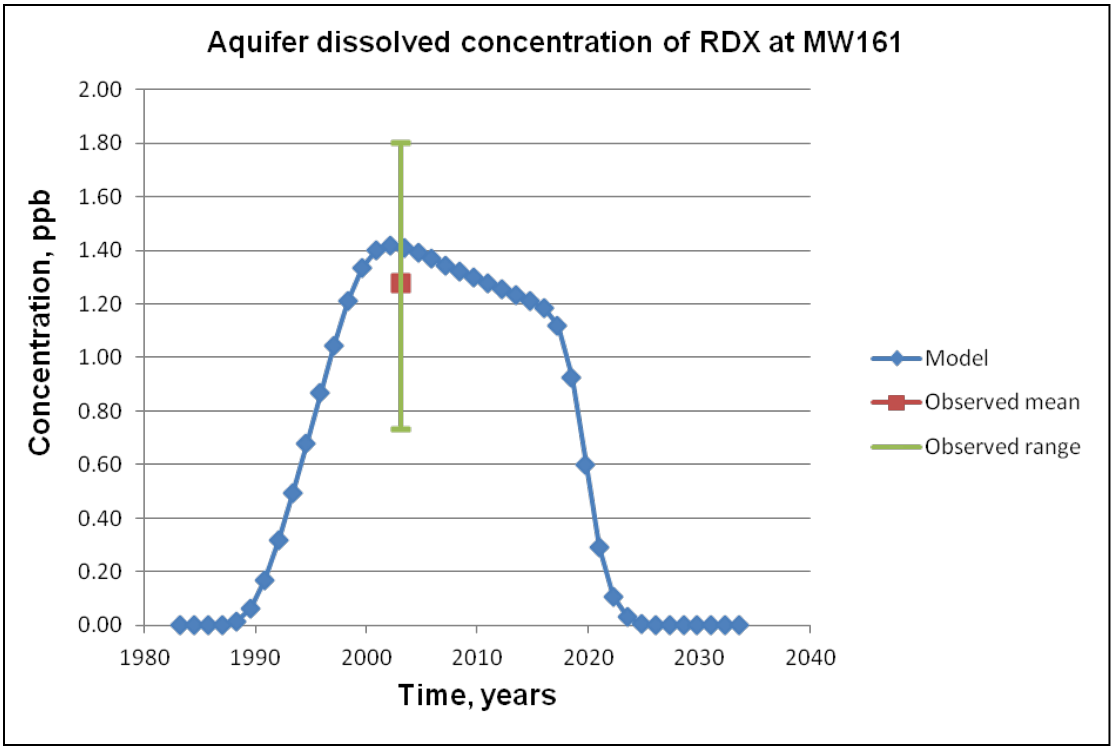

Figure 11. Computed and Observed RDX Aquifer Concentrations at MW161 Down-gradient of MMR Demo Area 2.

Figure 11 shows the results of running the soil model for 30 years; thus, after 30 years there is no flux of RDX mass from soil to vadose zone. The cessation of this flux causes the groundwater concentration of RDX to rapidly decrease toward zero after about 40 years. If the soil model is run longer, the soil concentrations of RDX persist over 100 years while gradually decreasing to zero over that period due to rather slow dissolution of solid phase RDX. Likewise, the RDX concentration in groundwater persists much longer, gradually decreasing towards zero over 120 years or longer. A gradual decrease is expected with a slowly dissolving source mass present.

During the mid-term progress review of this work unit, a member of the review panel recommended that the model be compared with more recent groundwater RDX observations at Demo Area 2. The remediation manager for the Camp Edwards Impact Area Groundwater Study Program of the Army National Guard was contacted to obtain data collected after 2004. As a result, all of the measured RDX concentrations in groundwater for Demo Area 2 were obtained. During the process of obtaining the additional data, it was learned that during 2004 the surface soil at Demo Area 2 was removed and treated to remove source mass of RDX. Thus, TREECS™ was reapplied to the site using the soil model BMP module. The model option *Source Removal BMPs/Selective MC Removal* was selected, and all remaining RDX mass in surface soil was entered for removal during 2004. RDX mass removed during 2004 was specified as 10,400 g in the model input. This mass was computed using the computed surface soil concentration in 2004 of about 1.5 mg/kg times the AOI surface soil volume times the soil dry bulk density.

The results of the reapplied model are shown in Figure 12 along with all of the observed RDX groundwater concentrations measured at MW-161 from 2001 through 2015. Model results are presented for the two cases of with- and without-source RDX, mass-removed in 2004. As shown by the figure, aquifer RDX concentrations persist longer without source removal. The observed RDX concentrations vary widely over time in practically a random manner, although there appears to be a slightly downward trend over time. Some of this variation could be caused by time-varying rainfall and resulting aquifer recharge. Such flow fluctuations can cause fluctuating RDX concentrations due to pulsing mass loading from soil and through the vadose zone, varying amounts of aquifer dilution, and varying plume elevations (and thus concentrations) associated with time-varying flow and water table elevation fluctuations. The MEPAS groundwater models use steady-state (long-term average annual) water flows, so it is not possible to predict any transient behavior associated with time-varying aquifer recharge. Thus, the model provides concentrations that vary more gradually as associated with long-term average annual hydrology. The mean of the observed RDX data for time and concentration is plotted in Figure 12, and the model agrees quite well with this mean. It will be interesting to see if the observed concentrations drop over the next few years as the model indicates that they should.

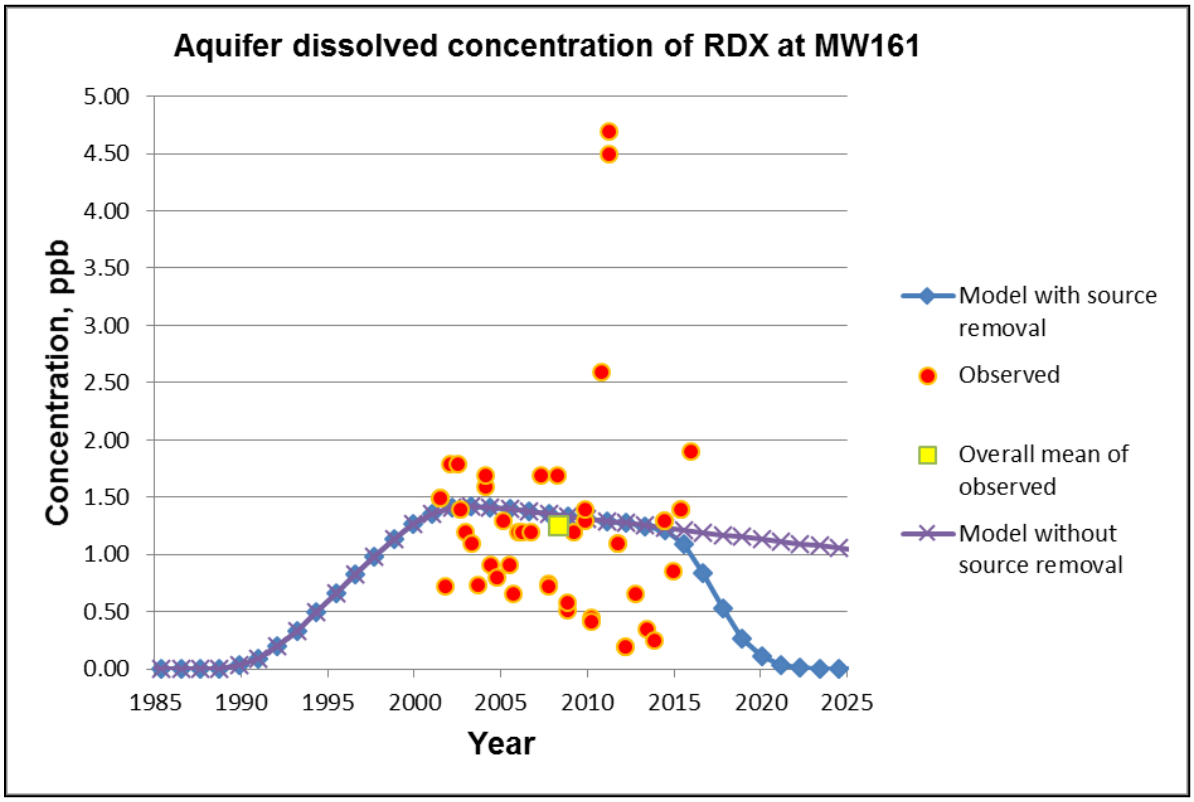

Figure 12. Computed (with and without source removal) and Observed (2001–2015) RDX Aquifer Concentrations at MW161 Down-gradient of MMR Demo Area 2.

6.4 UNCERTAINTY ANALYSIS

A sensitivity analysis of various model inputs and their effect on peak RDX concentration at MW161 is discussed by Dortch (2015) for this study site. That study evaluated the effects of uncertainty in the following inputs: RDX residue loading rate; average size of unexploded, solid-phase RDX particles; location of the monitoring well relative to the expected RDX plume centerline in groundwater; and dispersivity factors for groundwater dispersive transport. Model results were sensitive to all the above model inputs, which were substantially uncertain, site specific, and physically based.

There are other site-specific inputs for the three TREECS™ models used in this application, (e.g., soil texture/composition, meteorology, etc.); however, most of those inputs are much better known or estimated and are not discussed here. None of the uncertain inputs discussed above are chemical-specific. The remainder of this section focuses on the two chemical-specific inputs that were determined to be sensitive with some uncertainty; these included the soil-water linear, adsorption, partitioning, distribution coefficient (K_d, L/kg) and the half-life (which is related to the degradation rate) in the vadose zone. Solubility, another chemical-specific input, affects the particle dissolution rate, but solubility of RDX is well known. The Henry's Law constant (HLC) is a chemical-specific input that affects volatilization loss, but values for it are either known or can be reliably estimated with models, such as those included in the EPI Suite software developed by the U.S. EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation (http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm). The EPI Suite can also be accessed through CTS. Furthermore, HLC for RDX is so small (6.23E-8 atm-m^3/mole), there is practically no volatilization.

The half-lives of RDX in soil and groundwater are highly uncertain inputs, but their values are expected to be high in this application. RDX does not readily degrade in aerobic systems (Speitel et al. 2001; Hawari 2000). The soil, vadose zone, and even the groundwater at Demo Area 2 of MMR are aerobic. Half-lives of RDX on the order of years and much longer are reported for aerobic systems (Speitel et al. 2001; Ronen et al. 2008). An RDX half-life of 100 years was used in the validated model for soil, vadose zone, and groundwater. Only dissolved phase RDX in soil pore water and groundwater was allowed to decay in this study. An RDX half-life in AOI surface soil of a year and higher had little to no effect on groundwater concentrations for this study site due to the relatively short retention time of dissolved RDX in the surficial soil layer. Similarly, a half-life of a year or more in groundwater had no effect on groundwater concentrations at this site due to the relatively short travel time of about two months in the groundwater below the source zone to MW161. However, the travel time through the vadose zone from surface soil to the water table is approximately 12 years as determined from the model. Thus, half-lives for the vadose zone of less than 100 years have a profound effect on groundwater concentrations. Half-lives greater than 100 years produced results very similar to those obtained using a 100-year half-life. For example, assuming no degradation in the vadose zone resulted in a peak groundwater concentration of RDX at MW161 of 1.54 ppb compared with 1.42 ppb for a 100-year half-life, which was the value used for the validated model.

Higher values of K_d cause greater retardation of constituent transport, which for this study site results in attenuation of the groundwater concentration versus time curve, exhibiting a rounder curve that peaks later at lower concentration. The soil K_d values for organic chemicals can be estimated within the model user interfaces (UIs) based upon the organic carbon normalized soil–water sorption partition coefficient K_{oc}, the soil class (e.g., silty loam), which sets the percent sand, silt, and clay, and the percent organic matter content. The surface soil class at the study site is silty loam, whereas the below-ground surface (bgs) soil class required for vadose zone and aquifer modeling is sand. The values used for organic matter content of surface soil and bgs soil were 1.7% and 0.17%, respectively. The recommended value of K_{oc} is 13.2 L/kg based upon a measured value in one of the TREECS™ constituent databases. These inputs result in an estimated K_d of 0.203 L/kg for surface soil and 0.024 L/kg for bgs soil; these two values were used for the validated soil and vadose/aquifer models, respectively. Since the model UIs use K_{oc} to estimate K_d, K_{oc} is actually the uncertain input. Values of K_{oc} for RDX provided by EPI Suite in CTS were 51.7 and 89.1 L/kg. Estimates for K_{oc} were considered to vary between approximately 4.6 to 195 L/kg based on values within the TREECS™ three constituent databases and estimates from CTS.

Sensitivity and uncertainty analysis is provided within TREECS™ using Monte Carlo simulation with Latin Hypercube sampling. The user specifies the uncertain input variables and the statistical distributions describing their variability. The sampled output variables are also specified. Uncertainty analysis was conducted separately for RDX half-life in the vadose zone and K_d for surface and bgs soil. These two analyses are discussed below.

The half-life of RDX in the vadose zone was treated as uncertain with a mean value of 100 years and upper and lower bounds of 300 and 5 years, respectively. A log uniform distribution was assumed since the bounds are so large and there is no clearly known value for half-life; thus, values should receive equal consideration within the entire range of values. The Monte Carlo simulation was set to 100 iterations, although results converged within about 60 iterations. The model results for RDX aquifer concentration versus time at MW161 are compared with the mean and range of observed concentration as shown in Figure 13. This plot is similar to that shown in Figure 11, except that the upper and lower 95% uncertainty confidence bands are included in the plot. The observed RDX concentrations and upper confidence limit shown in Figure 13 tend to support the use of a rather high half-life.

The soil-RDX partition coefficients K_d for soil, vadose zone, and groundwater were treated as uncertain, with a mean value of 0.203 L/kg for soil and 0.024 L/kg for vadose zone and groundwater. A log uniform distribution was used with upper and lower bounds of 0.071 and 3.0 L/kg, respectively, for soil K_d, and upper and lower bounds of 0.0084 and 0.36 L/kg for K_d of the vadose zone and aquifer. These K_d values were estimated via the tools within the model UIs and using upper and lower bound K_{oc} values of 4.6 and 195 L/kg. The Monte Carlo simulation was run for 100 iterations. The model results for RDX concentration versus time at MW161 are compared with the mean and range of observed concentration, as shown in Figure 14 with the inclusion of the upper and lower 95% confidence limits, due to uncertainty of K_d in soil and groundwater.

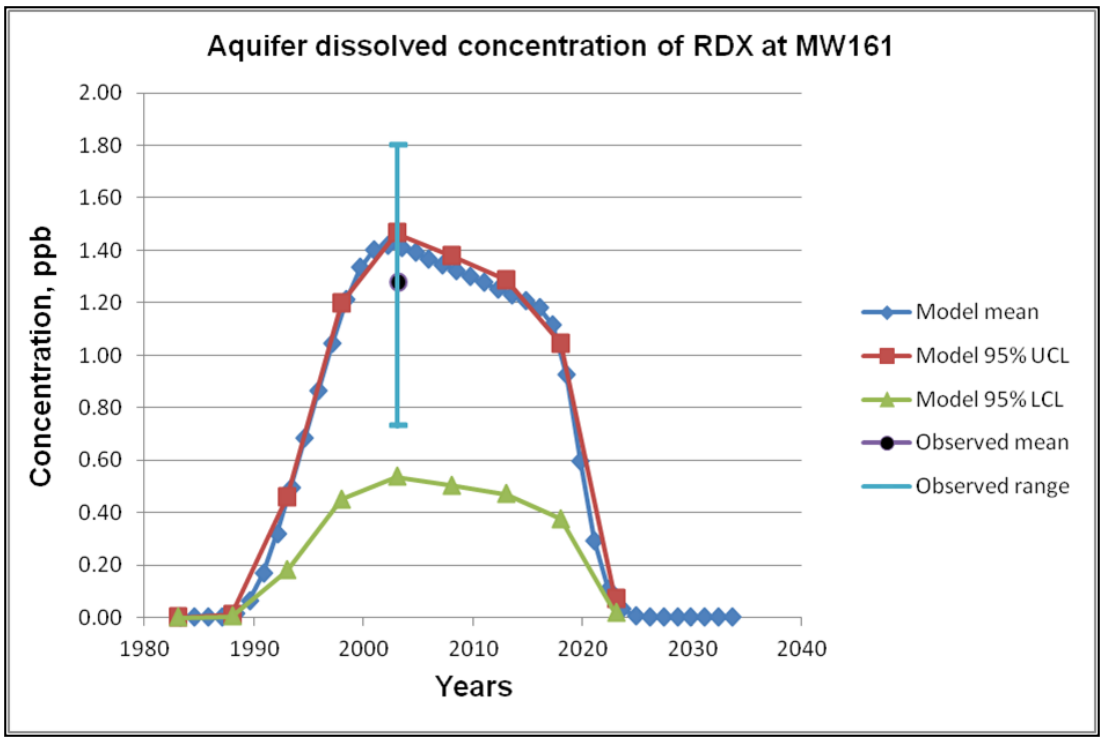

Figure 13. Computed and Measured Groundwater Concentrations of RDX at MW161 Down-gradient of Demo Area 2 with Upper (UCL) and Lower (LCL) Confidence Limits for Uncertainty on RDX Half-life.

The lower confidence limit (LCL) in Figure 14 is much farther from the model mean (validation) than the upper confidence limit (UCL) due to the much longer transit time through the vadose zone associated with high K_d values. The longer transit time allows for greater degradation of RDX. The confidence limits in computed soil concentrations of RDX, which are not presented, were very close to the model validation result shown in Figure 10, indicating variations in the soil K_d had a minor effect on model results for this application. An additional uncertainty run was made where only the K_d value for vadose zone was treated as uncertain. The confidence limits for this run were very similar to those shown in Figure 14, thus reinforcing the conclusion that model results are sensitive to vadose zone K_d values but insensitive to surface soil and groundwater values for this application. Likewise, model results are sensitive to vadose zone half-life of RDX but relatively insensitive to surface soil and groundwater values due to the relatively short transit times in those media. The uncertainty bands bracket the mean of the observed data, thus satisfying the second performance objective.

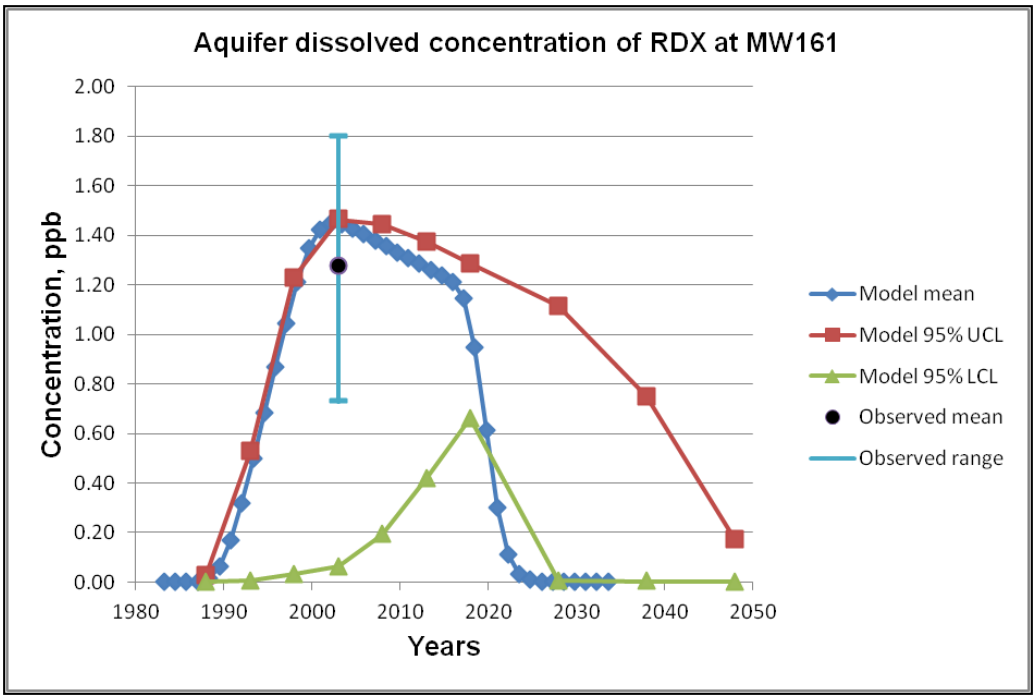

Figure 14. Computed and Measured Groundwater Concentrations of RDX at MW161 Down-gradient of Demo Area 2 with Upper (UCL) and Lower (LCL) Confidence Limits for Uncertainty on RDX K_d in Soil and Groundwater.

6.5 FATE OF EMERGING MC (EC) ASSOCIATED WITH IM

The five MCs – DNAN, NTO, NQ, AP, and CL-20 – were selected within the TREECS™ validation application of Demo Area 2 for evaluating their fate relative to that of RDX. Each of these five MCs are referred to as an EC for brevity. The inclusion of these five additional ECs in the application required specifying their physicochemical properties, which are not as well-known as those of RDX. The EPI Suite component of CTS was used to provide some of the properties information for the five ECs, such as HLC and K_{oc} values. Besides specifying the physicochemical properties and the partitioning distribution coefficients in soil for the EC, the only other additional input that was required was the residue loading rate for each EC, which was set to the same rate as that of RDX, or 1,500 g/yr, and degradation half-life in each media. All other model inputs were the same as the validation application (Dortch et a. 2017).

6.5.1 Initial inputs and results

Inputs were initially set using the best available information within TREECS™-CTS without exerting any additional study or literature review, thus relying on default methods within the systems. The EC-specific model inputs that were used initially are shown in Table 3. Ammonium perchlorate was declared as miscible due to its very high solubility. The degradation half-life and initial solid-phase particle size was assumed to be the same as that of RDX for comparison purposes. Less is known about the degradation rates of these ECs than is known for RDX, and CTS does not provide estimates for biotic degradation rates. Thus, retaining the same half-lives as for RDX was the only rational alternative.

Table 3. EC-specific Model Inputs for Demo Area 2 Application.

Input Description	DNAN	NTO	NQ	AP	CL-20
Fate/Transport Parameters					
Surface soil soil-water constituent partition coefficient, K_d, L/kg, computed by soil model UI from K_{oc}, soil texture, and percent organic matter for all except CL-20	2.43	1.93	0.18	2.0E-4	2.0[1]
Vadose/aquifer soil-water constituent partition coefficient, K_d, L/kg, computed by model UI from K_{oc}, soil texture, and percent organic matter for all except CL-20	0.29	0.23	0.022	2.9E-5	0.2[2]
Decay/degradation half-life of aqueous phase constituent, years	100	100	100	100	100
Decay/degradation half-life of adsorbed (particulate) phase constituent, years	1.0E20	1.0E20	1.0E20	1.0E20	1.0E20
Initial mean diameter of solid phase constituent residue particles (assume spherical particles), µm	6,000	6,000	6,000	NA miscible	6,000
Volatilization rate, m/yr, as computed by soil model UI from molecular diffusivity in air	42.5	65.3	65.8	0 miscible	28.6
Chemical-Specific Properties					
K_{oc}, L/kg	158.5[a]	125.9[a]	12[b]	0.016[c]	2.7[d]
Molecular weight (molar mass or averaged molecular mass), g/mol (all from NIST[e])	198	130	104	117.5	438
Aqueous solubility limit, mg/L	276[f]	16,600[g]	3,800[h]	249,000[i]	4.33[j]
Henry's Law constant, atm-m^3/g-mol	3.01E-7[k]	4.07E-13[l]	4.49E-12[l]	0	9.39E-25[m]
Solid phase constituent mass density, g/cm^3 (all values except CL-20 were cited by Taylor et al. 2015, which agree with values found via Internet searches)	1.34	1.93	1.72	1.95	2.04[n]
Molecular diffusivity in air, m^2/day (all estimated from method by Fuller et al. 1966)	0.56	0.86	0.87	NA Non-volatile	0.37

[1] Mean of range of values reported by Szecsody et al. (2004) for soil
[2] A factor of 10 lower than soil K_d due to organic matter being lower by a factor of 10
[a] Estimated, Chakka et al. 2010
[b] Average of values estimated with EPI Suite using the MCI and K_{ow} methods; agrees with estimated value from Hazardous Substances Data Bank (HSDB), http://toxnet.nlm.hih.gov
[c] Estimated from $K_{OC} = 23.83 K_{OW}^{0.544}$ with K_{ow} = 1.45E-6 obtained from EPA (2008)
[d] Chemspider (http://www.chemspider.com/) predicted from ACD/Labs Percepta Platform - PhysChem module
[e] National Institute of Standards and Technology (NIST), http://www.nist.gov/
[f] Measured, Boddu et al. 2008
[g] Interpolated from measured, Spear et al. 1989
[h] Haag et al. 1990
[i] Agency for Toxic Substances and Disease Registry (ATSDR), http://www.atsdr.cdc.gov/
[j] Karakaya et al. (2003)
[k] Estimated with EPI Suite group method
[l] Estimated with EPI Suite bond method
[m] Chemspider http://www.chemspider.com/) predicted from EPI Suite, bond method
[n] Hoffman (2003)

A wide range of values for K_{oc} was found for CL-20, thus introducing high uncertainty in estimated K_d values. Therefore, the K_d value for CL-20 in surface soil was set to the mean of the range of values reported by Szecsody et al. (2004) for aerobic soil. The K_d for CL-20 in vadose zone and groundwater was set to a factor of 10 lower than for surface soil due to the organic matter being a factor of 10 lower.

The soil model was run for 100 years rather than 30 years so that the results for groundwater could be protracted. The computed groundwater concentrations at MW161 for the five EC are plotted versus time in Figure 15 along with the results for RDX. The low solubility of RDX relative to four of the other MC causes RDX concentrations to persist longer but at lower concentrations. There is still considerable mass of RDX in soil after 60 years, whereas four of the five ECs have been dissolved and nearly totally flushed out of the soil. Four of the five ECs are transported out of the system faster than RDX, but this occurs with a price of greater peak groundwater concentrations. DNAN and NTO are attenuated more than NQ and AP due to their higher K_d values.

The EC CL-20 persists in soil well after 100 years since it has the lowest solubility of all six MCs. The peak groundwater concentration of CL-20 is more than an order of magnitude lower than the other MCs due to its very slow migration, associated with its low solubility. The low solubility of CL-20 could make it a good candidate as a future HE due to its lower concentration in receiving waters.

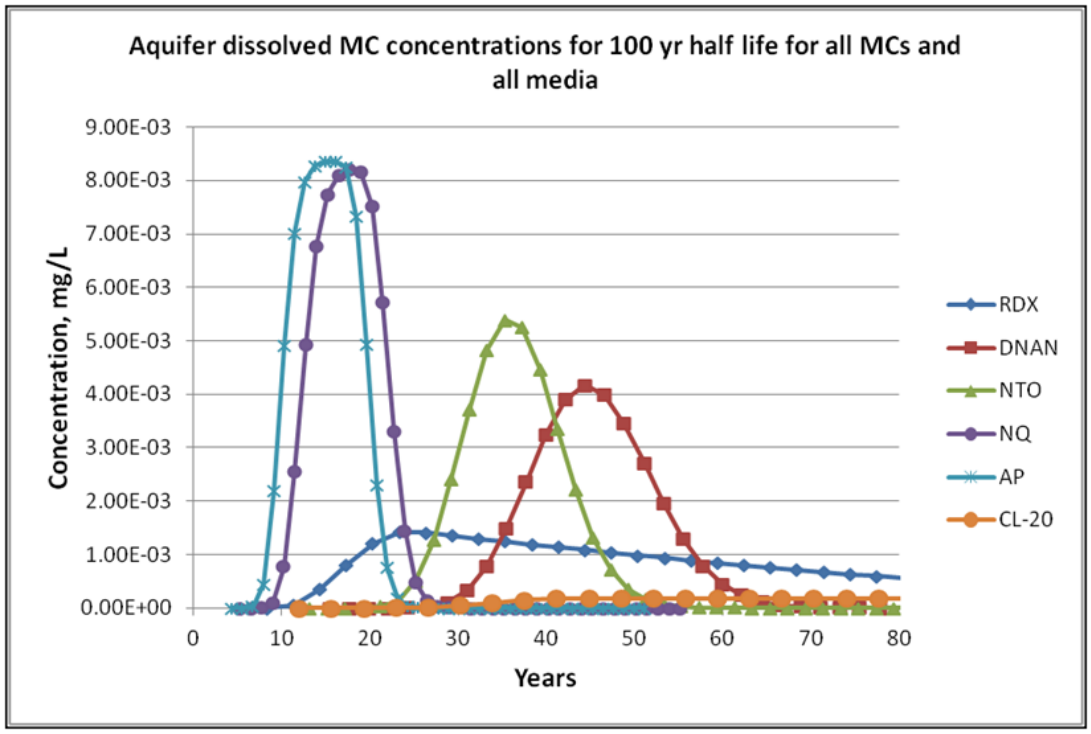

Figure 15. Computed Aquifer Concentrations at MW161 Down-gradient of Demo Area 2 for Five ECs and RDX with Half-life of 100 years for all MCs in all Media.

6.5.2 Refined inputs and simulation results for DNAN and NTO

Additional attention is given to the fate of DNAN and NTO due to the interest in using these two explosive components as potential replacements for TNT and RDX, respectively. There is also uncertainty regarding their properties associated with fate processes. As a result, the physicochemical properties of these MCs are evaluated in greater detail, and the effects on their fate due to refinement in those properties are presented below.

There is relatively high confidence in the values for molecular weight, water solubility, and solid phase density of DNAN and NTO. Although there is some uncertainty in the HLC, values are so low that volatilization is a very minor fate process. Likewise, diffusivity in air, which is an input used to compute volatilization, has low importance. Elimination of these input variables leaves only the soil partitioning coefficient K_d and the degradation rates as important and uncertain MC-specific inputs.

Unlike most HE, NTO can have a lower adsorption to soils due to its negative charge at environmentally relevant pH values, and it may not correlate well to soil organic carbon (OC) content (Dontsova et al. 2014). The K_d for DNAN and NTO shown in Table 3 were computed based on the input values for K_{oc}, the soil texture (e.g., silty loam), and the soil organic matter content. The input values of K_{oc} for DNAN and NTO in Table 3 were computational derived from K_{ow} by Chakka et al. (2010), which can be unreliable, particularly for polar compounds.

Dontsova et al. (2014) have measured batch K_d values for DNAN and NTO using 11 different soils with widely varying properties. These soils vary from loams with mostly sand, to clay loam with 32% clay. The soil pH ranges from 4.23 to 8.21, and OC content ranges from 0.34% to 5.28%. The surface soil at Demo Area 2 is silty loam with a pH of 4.6 and organic matter content of 1.7% (AMEC Earth Environmental 2004). Organic matter is generally about 40% OC. The deeper soils of the vadose zone and aquifer of Demo Area 2 are mostly sand with one order of magnitude lower organic matter content (i.e., 0.17%) and pH of about 5.9. Silty loam generally has a texture of 20-65-15% sand-silt-clay. Sand texture is generally 92-5-3% sand-silt-clay.

The characteristics of the 11 soils used in the Dontsova et al. (2014) study were reviewed in an attempt to match as closely as possible the particular soil to the soil texture and pH at Demo Area 2. Matching the soil OC content was considered less important since the measured K_d values were normalized to OC to provide K_{oc}. The soils that are the most similar to the surface soils at Demo Area 2 are Catlin (Urbana, IL), Arnold AFB (Arnold Air Force Base, TN), Sassafras (Aberdeen Proving Ground, MD), and Plymouth (MMR, MA). Of course, the Plymouth site is at the same installation as Demo Area 2, but its texture is closer to that of the deeper soils at Demo Area 2.

The characteristics of these four soils and the corresponding measured batch K_d and OC normalized K_{oc} values for DNAN and NTO are shown in Table 4 along with the R^2 of the fit for K_d. The model values of K_d and K_{oc} for DNAN in surface soil of 2.43 and 158.5 L/kg, respectively, in Table 3 agree reasonably well with the measured values in Table 4, which range from 1.89 to 5.95 L/kg for K_d and 113 to 179 L/kg for K_{oc}. However, due to the low organic matter content, the estimated DNAN K_d value of 0.29 L/kg for sub-surface soil in Table 3 is an order of magnitude lower than the range of measured values in Table 4. It is noted that the OC content of the four soils in Table 4 ranged between 1.3% for Sassafras to 5.28% for Catlin, which is much higher than the OC content of the sub-surface soils at Demo Area 2.

The K_{oc} of the four soils averages 140.7 L/kg for DNAN. If this value is multiplied by the fraction of OC content of the Demo Area 2 sub-surface soil (which is about 0.00068), then the estimated K_d is 0.096 L/kg, which is about the same order of magnitude as the value estimated from the MEPAS model UI of 0.29 L/kg. Thus, the low model K_d value for sub-surface soil seems reasonable given the very low OC content of those soils. Overall, the values of K_d used in the original modeling of DNAN seem quite reasonable. Thus, the original K_d values for DNAN of 2.43 and 0.29 L/kg for surface and sub-surface soil, respectively, were used for the improved simulation.

Table 4. Soil Characteristics, Measured Batch K_d, and Corresponding K_{oc} Values for DNAN and NTO for Four Soils Similar to Demo Area 2 Soils (Dontsova et al. 2014).

Soils	Sand-silt-clay, %	Soil pH	DNAN K_d, L/kg	R^2, DNAN K_d	DNAN K_{oc}, L/kg	NTO K_d, L/kg	R^2, NTO K_d	NTO K_{oc}, L/kg
Catlin	9-65-26	7.31	5.95	0.92	113	0.21	0.92	3.98
Arnold AFB	23-66-11	6.66	3.39	0.78	126	0.34	0.94	12.69
Sassafras	41-42-17	4.40	1.89	0.72	145	0.48	0.96	36.92
Plymouth	75-20-5	4.23	4.38	0.94	179	0.50	0.96	20.41

The values of K_d and K_{oc} for NTO of 1.93 and 125.9 L/kg, respectively, in Table 3 are about an order of magnitude higher than the measured values in Table 4, which range from 0.21 to 0.5 L/kg for K_d and 3.98 to 36.92 L/kg for K_{oc}. Also, the relative range in K_{oc} for NTO is much greater than it is for DNAN indicating less correlation of partitioning to OC content for NTO. Partitioning of NTO to soil appears to be more closely associated with soil pH with an inverse relationship (Dontsova et al. 2014). An NTO K_d value of about 0.5 L/kg seems far more appropriate for Demo Area 2 surface soil than the value of 1.93 L/kg that was used originally. With a higher pH in sub-surface soil of 5.9, the K_d in that region of Demo Area 2 is likely in the range between 0.34 to 0.48 L/kg. Thus, the value of 0.23 L/kg that was originally used in the modeling is not so unreasonable. In retrospect, K_d values for NTO of 0.5 and 0.4 L/kg for surface and sub-surface soils, respectively, are more appropriate for Demo Area 2; thus, these values were used for the improved simulation.

Although there are recent studies of degradation of DNAN and NTO in enriched cultures, there is little information regarding degradation rates of these two MC in natural environmental settings. Information regarding the potential for degradation can be gleaned from CTS, but actual degradation rates cannot be predicted by CTS. Degradation half-lives for DNAN and NTO on the order of a few days to a week were reported by Dontsova et al. (2014) for their batch laboratory studies, and they reported even shorter half-lives for NTO in their soil column flow studies.

Perreault et al. (2012) studied the aerobic biotransformation of DNAN using artificially contaminated soil microcosms. DNAN was completely transformed in 8 days in soil slurries supplemented with carbon and nitrogen sources. DNAN was completely transformed in 34 days in slurries supplemented with carbon sources alone. However, DNAN persisted with little degradation in the unamended microcosms. A strain of *Bacillus* (named 13G) in the soil was determined to transform DNAN by co-metabolism (Perreault et al. 2012). Similarly, Fida et al. (2014) were able to aerobically biodegrade DNAN by *Nocardioides* sp. (strain JS1661), which was isolated from activated sludge.

Although Perreault et al. (2012) stated that DNAN persisted in the unamended microcosms, there was some small amount of DNAN loss that can be observed in their concentration versus time plot. The slow rate of degradation of DNAN presented by Perreault et al. (2012) for the un-amended microcosm was estimated to have a half-life of about 0.6 years, which is probably more representative of degradation in natural aerobic environments, such as Demo Area 2. Thus, for the improved simulation, it was assumed that DNAN has a half-life of 0.6 years in surface and sub-subsurface soil.

Krzmarzick et al. (2015) were able to readily reduce NTO anaerobically in microcosms using inoculated microbial communities from seven different soils. However, NTO was non-biodegradable in aerobic microcosms with all seven soil inoculated communities. These results are similar to those for RDX, where RDX is degraded under anaerobic conditions but degrades very slowly for aerobic conditions. As with DNAN, microbial enrichment techniques have been used to biodegrade NTO rather rapidly for aerobic conditions. For example, Richard and Weidhaas (2014) showed simultaneous aerobic degradation within 4 days for IM components DNAN, NTO, and NQ in the explosive formulation IMX 101 using soil enrichment cultures involving sludge, soil, and compost. However, for natural aerobic environments like Demo Area 2, it is probably best for now to assume that NTO degrades similarly to RDX. Thus, for the improved simulation, it was assumed that NTO has a half-life of 100 years for surface and sub-surface soil, which is the same as for the initial simulation of the IM components.

In summary, the improved simulation for the EC DNAN and NTO maintained the same inputs as the original simulation with the exception that the K_d values for NTO were changed from 1.93 and 0.23 L/kg to 0.5 and 0.4 L/kg for surface and subsurface soil respectively, and the degradation half-life of aqueous phase DNAN was changed from 100 years to 0.6 years for all media (soil, vadose, and aquifer).

The aquifer concentration results at MW161 for the improved simulation of DNAN and NTO are not plotted but are described as follows. The concentration of DNAN was essentially zero in the aquifer due to the relatively fast degradation rate associated with the lengthy transit time through the vadose zone. The concentration versus time curve for NTO was practically the same as that shown in Figure 15. Even though the K_d for NTO in surface soil was considerably lower than it measured originally, the high solubility coupled with the relatively short retention time in soil translated into only a very minor effect on flux from soil to vadose zone and resulting aquifer concentrations. Thus, the simulation of improved inputs for DNAN and NTO exhibited no change for NTO and major change for DNAN with essentially zero DNAN present in groundwater. Given that DNAN is similar to TNT and NTO is similar to RDX, it is not surprising that DNAN, like TNT, could potentially be absent in groundwater when NTO, like RDX, could often be present. This application demonstrates the need for better methods and more research for estimating degradation rates in natural environmental media.

6.6 BMP ASSESSMENT

The term best management practice (BMP) is used loosely here to include any management alternative, including remediation strategies, that reduces future concentrations of MC in down-gradient receiving waters. Three BMPs, or remediation strategies, were evaluated for reducing aquifer concentrations of RDX: surface soil amendment to increase adsorption of RDX to soil; surface soil amendment to increase degradation rate (decrease half-life) of pore water RDX; and groundwater injection to increase degradation rate of RDX in the aquifer plume. Two half-lives were tested for the surface soil amendment to increase degradation rate.

RDX adsorption correlates more closely with clay content than with organic matter content of soils (Boyer et al. 2007). Thus, clay could be added to surface soils at Demo Area 2 to increase the soil-pore water sorption partition coefficient, K_d. It was assumed for comparison purposes that K_d of the surface soil could be increased by a factor of 10 from a value of 0.203 L/kg as used in model validation to a value of 2.03 L/kg. All other inputs for the soil model as well as those of the vadose and aquifer models were kept the same as the validation inputs. As shown in Figure 16, the results of this first BMP (BMP 1) were practically identical to those of the validation application. In other words, there was no reduction in aquifer concentrations of RDX, only a slight delay in aquifer concentrations compared with the base condition (i.e., the validation result). This BMP causes the surface soil to hold RDX a little longer, but this effect alters the groundwater concentrations very little.

For BMP 2, it was assumed that an amendment, such as rich organic matter with microbes, is added to the surface soil to increase biological degradation of RDX, thus decreasing the half-life to about one month or to 0.1 year. Therefore, the aqueous-dissolved RDX half-life in soil was changed from 100 years to 0.1 year and all other inputs remained the same as the base (validation condition). The results of BMP 2 are shown in Figure 16 for aquifer concentration at MW161 compared to the base results. As the figure shows, the peak RDX concentration is reduced from about 1.4E-3 mg/L (1.4 ppb) to about 0.9 ppb. Greater reductions in RDX concentration do not occur due to the relatively short residence time of RDX in surface soil pore water. The rapid drop in RDX concentration after 110 years is due to running the soil model for only 100 years.

A variation of BMP 2 was run where the surface soil aqueous dissolved RDX half-life was reduced further. Enhanced RDX degradation and transformation can be achieved with hydrated lime (calcium hydroxide, as well as quicklime calcium oxide) added to the soil that induces alkaline hydrolysis (Larson et al. 2008; Johnson et al. 2011) to abiotically transform RDX and other HE. Alkaline hydrolysis via soil liming produced a degradation half-life of 2,592 minutes (0.005 year) for RDX on a grenade range at Ft. Lewis, WA. (Johnson et al. 2011). The dissolved phase RDX half-life in soil was set to 0.005 year for BMP 2a. The results of this test are shown in Figure 16 along with the base results for comparison. The peak RDX aquifer concentration is reduced by more than a factor of 10 to 0.11 ppb for BMP 2a.

The third BMP involved reducing the RDX half-life in groundwater from 100 years to 0.1 year. Such a reduction is feasible through injection of organic substrate and microbes into the groundwater RDX plume to reduce RDX via enhanced biodegradation. All other model inputs were the same as the validation or base condition. The results of BMP 3 are shown in Figure 16. BMP 3 has the effect of reducing RDX concentrations at MW161 from about 1.4 ppb to 0.4 ppb.

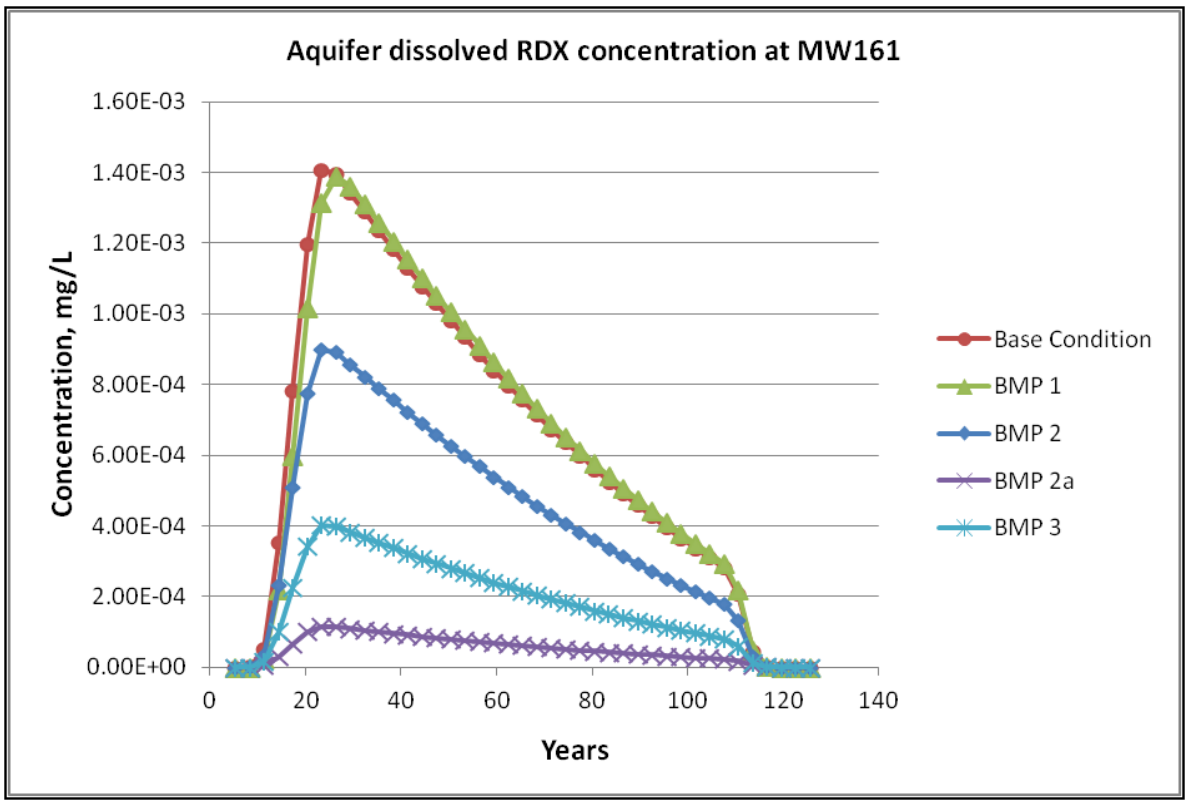

Figure 16. Computed Aquifer Concentrations of RDX at MW161 Down-gradient of Demo Area 2 for Four BMPs Compared to Base Condition.

Since it is difficult to immobilize the movement of RDX in water, the more promising BMP or remediation strategies involve degradation, or reduction, of RDX. The BMP tests conducted here show that RDX reduction strategies could be beneficial when applied only to the surface soil or only within the aquifer. It is noted that the degradation BMPs in soil require implementation before RDX has migrated to the vadose zone and groundwater, which was the assumption in these BMP applications. An RDX reduction strategy was not applied to the vadose zone due to the perceived high costs of implementing such a strategy, thus making the practicality of such an alternative questionable. These BMP applications demonstrate that TREECS™ can be applied to assess the potential effectiveness of various BMP strategies.

7.0 PERFORMANCE ASSESSMENT

The performance objective ratings are summarized in Table 5 for the application to MMR Demo Area 2, in Table 6 for the application to the AIA of USMA, and in Table 7 for the application to the ZIA of Camp Pendleton. A discussion of each performance objective rating for all three sites follows in the sections below.

Table 5. Performance Objectives Success Ratings for MMR Demo Area 2 Application.

Performance Objective	Success Rating
TREECS™ accurately simulates long-term fate of MC on ranges	Highly successful: model concentrations were less than a factor of 3 of observed for soil and aquifer
TREECS™-CTS can be used to quantify uncertainty in inputs	Successful: model uncertainty results bracketed observed field MC concentrations at the 95% confidence level
TREECS™-CTS can be quickly set up and run with readily available data	Successful: TREECS™, including CTS use, was set up and validated in 8 labor hours, far less than the criteria of 80 hours
Training requirements are reasonable	Training has not yet occurred.
TREECS™-CTS can be applied to evaluate range management and/or remediation strategies	Successful: TREECS™ was used to evaluate three BMP strategies to reduce RDX concentrations in groundwater
TREECS™-CTS can be applied to evaluate the fate of emerging MC	Successful: TREECS™-CTS was applied to evaluate the fate of DNAN, NTO, NQ, AP, and CL-20 with comparison to results for RDX

Table 6. Performance Objectives Success Ratings for AIA Application.

Performance Objective	Success Rating
TREECS™ accurately simulates long-term fate of MC on ranges	Highly successful: model concentrations were less than a factor of 3 of observed for Popolopen Brook on three different dates
TREECS™-CTS can be used to quantify uncertainty in inputs	Moderately successful: model uncertainty results bracketed observed field MC concentrations at the 95% confidence level for one of the three observation dates
TREECS™-CTS can be quickly set up and run with readily available data	Successful: TREECS™, including CTS use, was set up and validated in 16 labor hours, far less than the criteria of 80 hours
Training requirements are reasonable	Training has not yet occurred.
TREECS™-CTS can be applied to evaluate range management and/or remediation strategies	Successful: TREECS™ was used to evaluate three BMP strategies to reduce RDX concentrations in surface water
TREECS™-CTS can be applied to evaluate the fate of emerging MC	Successful: TREECS™-CTS was applied to evaluate the fate of DNAN, NTO, NQ, AP, and CL-20 with comparison to results for RDX

Table 7. Performance Objectives Success Ratings for ZIA – Las Flores Watershed Application.

Performance Objective	Success Rating
TREECS™ accurately simulates long-term fate of MC on ranges	Highly successful: model concentrations were less than a factor of 3 of observed for Las Flores Creek and aquifer for one set of observations above detection
TREECS™-CTS can be used to quantify uncertainty in inputs	Moderately successful: model uncertainty results bracketed observed field MC concentration at the 95% confidence level for Las Flores Creek but did not bracket the observation for Las Flores aquifer
TREECS™-CTS can be quickly set up and run with readily available data	Successful: TREECS™, including CTS use, was set up and validated in 50 labor hours, less than the criteria of 80 hours
Training requirements are reasonable	Training has not yet occurred.
TREECS™-CTS can be applied to evaluate range management and/or remediation strategies	Successful: TREECS™ was used to evaluate three BMP strategies to reduce RDX concentrations in surface water and groundwater
TREECS™-CTS can be applied to evaluate the fate of emerging MC	Successful: TREECS™-CTS was applied to evaluate the fate of DNAN, NTO, NQ, AP, and CL-20 with comparison to results for RDX

7.1 VALIDATION ACCURACY

The validation performance objective at all three study sites is rated highly successful since model-computed media concentrations are within a factor of 3 of observed data in all cases. Very close agreement was obtained for AOI soil and aquifer concentrations at down-gradient of Demo Area 2, MMR. Remarkably close agreement was obtained for surface water downstream of ZIA, Camp Pendleton. Fairly good agreement was obtained for Popolopen Creek downstream of the AIA, USMA. The poorest agreement was for groundwater down-gradient of the ZIA. The primary reason for disagreement in predicted and observed surface water concentrations is related to using annual average rainfall and hydrology rather than daily rainfall and hydrology. Stream concentrations are highly transient depending on recent rainfall to trigger measurable stream values. Lack of sufficient information regarding monitoring well locations is a contributing factor to the greater disagreement in model and observed for the Las Flores aquifer at Camp Pendleton.

7.2 UNCERTAINTY ANALYSIS

The objective pertaining to uncertainty analysis was rate successful for Demo Area 2 site and moderately successful for the AIA and ZIA study sites. The latter two sites were less than fully successful due to the fact that not all observed data were captured within the 95% confidence bands of the model analysis. However, it is noted that the expanse of the confidence bands depends on the inputs regarding uncertain parameters, such as their distribution and bounds. In most cases, the bounds were not very well known, so they were assumed, such as halving and doubling the mean, or validation, input value. For this reason and in hind-sight, this performance objective should have been qualitative rather than quantitative since the primary objective was to demonstrate the use of this feature rather than to quantify its utility.

7.3 TREECS™-CTS SET-UP TIME

This performance objective was rated as fully successful for all three study sites since all times were less than 80 labor hours. Approximately eight labor hours were required to set up and conduct the validation application for Demo Area 2, MMR. However, this relatively low labor requirement is due to the fact that this site had been previously modeled with TREECS™; therefore, the site information had already been gathered, reviewed, and entered into the model. All that was required during the present validation application was to review all inputs, make a few corrections or changes, and plot results.

Approximately 16 labor hours were required to set up and conduct the validation application for AIA, USMA. However, this relatively low labor requirement is due to the fact that other sites at the USMA had been previously modeled with TREECS™ (Dortch 2012), so the site information had already been gathered and analyzed.

Approximately 50 labor hours were required to set up and conduct the validation application for ZIA, Camp Pendleton. This labor included gathering, review, and analysis of site information, obtaining and processing various data for soil properties and meteorology, setting up model inputs, validating the model, and writing up all sections of this report dealing with input data and model validation. This labor also included assessing model output and making adjustments to better represent the perceived hydrological conditions at this site, which included groundwater recharge from stream flow. This relatively small labor requirement is significant given all of the study components that were performed as listed above. This application validates that these systems can be applied well within 80 labor hours, thus demonstrating the relatively low man-power requirements for TREECS™-CTS.

7.4 TRAINING

The training objective had not been met at the time this report was written. This training is being planned for 2017.

7.5 BMP ASSESSMENTS

The performance objective pertaining to evaluating range management and remediation strategies (i.e., BMPs) was rated as successful for all three study sites. At least 3 BMPs were evaluated for RDX at all three sites.

7.6 EC FATE

The performance objective pertaining to evaluating EC fate was rated as successful for all three study sites. Five ECs were modeled, and results were compared with that of RDX at all three sites.

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8.0 COST ASSESSMENT

The ESTCP requires that a cost benefit analysis (CBA) be conducted for each demonstrated technology. The CBA for this project is accomplished by comparing the costs associated with applying TREECS™-CTS to the cost of an ORAP Phase II for a study site where monitoring was conducted to assess range environmental impacts. Operational range assessments require periodic evaluation of the potential for an MC source on range to reach an off-range receptor. If no source-receptor interaction exists, then the range is classified as *unlikely*. If a potential source-receptor interaction is believed to exist, the range is classified as *inconclusive* and the assessment progresses to the next phase (e.g., ORAP Phase II) in which a more detailed assessment must be conducted, such as field monitoring. The period for range re-evaluations is every five years as a minimum. Periodic site monitoring is currently the approach used to assess MC fate and the environmental risk down-gradient of *inconclusive* at DoD training ranges. Such monitoring is conducted by the Army for ORAP Phase II. The Air Force and Navy also conduct phased studies for assessing off-site migration of contaminants from their training ranges.

8.1 COST MODEL

TREECS™-CTS can usually be applied to a study site within 80 labor hours. Application includes review of available data, processing inputs, model set-up, model calibration/validation, scenario assessment or assessing PAL exceedance, and preparing written documentation of results. Although all three study site applications reported herein were conducted in less than 80 labor hours, 80 labor hours are used as the cost to apply TREECS™-CTS. This cost is compared with the average cost to conduct an Army ORAP Phase II study for a single study site. A study site is defined as a single source-receptor interaction. For example, costs associated with assessing the concentrations of a particular MC, such as RDX, in a pond down-gradient of an artillery impact area would constitute a single study site. Under ORAP Phase II, this cost would include sampling, laboratory analysis, and documentation of the impact in the Phase II report.

The cost to apply TREECS™-CTS is converted from labor hours to dollar costs as follows. A reasonable federal pay grade of GS-12 step 5 (2016 pay scale) is used, which is $79,554 per year for generic “rest of U.S.” with 2,080 hours in a year, or $38.25 per hour. This hourly rate is multiplied by a burden factor, which includes the hourly pay rate, plus benefits, plus organizational overhead. A burden factor of 3.0 is used, resulting in a total hourly cost of $114.74. With a labor requirement of 80 hours, the cost of TREECS™-CTS for a single study site is estimated as $9,179.

The cost of conducting monitoring as part of ORAP Phase II includes labor for field sample collection; travel costs to/from and while at the installation being sampled; material required for sample collection; laboratory analysis of samples to determine concentrations; and labor costs for assessment and reporting of results. A reasonable federal pay grade of GS-9 step 5 is used for labor of personnel to collect field samples. This pay grade, which is $54,855 per year (2016 pay scale) for generic “rest of U.S.” with 2,080 hours in a year, requires $26.37 per hour. This hourly rate is multiplied by a burden factor of 3.0, resulting in total daily cost of $632.94. Two field personnel are required for three days of travel and field sample collection associated with one AOI and its primary target receiving waters. Thus, the total cost of labor for field sample collection is estimated as $11,393. Travel cost of two people for three days, including air fare, rental car, lodging, and per diem, is estimated to be $3,000. Material needed for sample collection, handling, storage, and shipping is roughly $1,000.

Laboratory analysis cost associated with an HE, such as RDX, is about $50 per sample.[10] Assuming sampling of water at three locations, three times (wet, dry, and storm event) with three replicates each, results in 27 samples to be analyzed at a cost of $1,350. Approximately 20 hours of labor for a GS12 step 5 is required for assessment and reporting of the field sampling results for ORAP. All total, the cost for monitoring a single study site is estimated to be $19,038. This cost is more than double the cost of applying TREECS™-CTS for the same study site.

8.2 COST DRIVERS

The primary driver in considering whether or not to apply TREECS™-CTS to DoD ranges is access or availability of properly trained personnel for applying models. Such personnel should have some background in modeling and prior experience in applying models. Assuming such personnel are available, there are no other factors that should affect the decision to apply TREECS™-CTS given the relatively low cost. The use of a modeling system such as this will save money in the long term and provide valuable information with additional benefits (such as management alternative assessments) quicker and cheaper than relying solely on field sampling. Probably the best approach to ensure that qualified personnel are available for conducting the modeling is to utilize environmental contractors that have existing delivery order contracts within the DoD. Many of these contractor firms already have qualified modeling personnel on staff.

A secondary driver for use of TREES™-CTS at a particular site is whether an ORAP Phase II assessment is required. If Phase II is required, then modeling should be performed to reduce costs for Phase II and to provide greater understanding of current and future environmental consequences. Provided that sampling is to be conducted in Phase II, modeling will provide improved insight for sample design, thus potentially reducing sampling costs while improving sampling quality and providing supplemental exposure information.

8.3 COST ANALYSIS

Currently, ORAP Phase II assessments have been required at approximately 100 installations.[11] Assuming three study sites per installation, a cost savings of about $10,000 per study site (rounding up of the cost savings of $9,858, which is probably low due to the unexpected costs of field data collection) results in a cost savings of about $3,000,000 per five-year re-evaluation that is required under ORAP. (This figure was computed by multiplying $10,000 by 3 and then by 100). However, the benefits of using TREECS™-CTS go far beyond the cost savings associated with modeling versus monitoring. Modeling can be used to forecast not only if PALs will be exceeded but when they will be exceeded. Additionally, the modeling system can be used to assess BMP strategies for avoiding future PAL exceedance and to evaluate the carrying capacity of existing and future ranges. Modeling allows the assessment of “what if” scenarios without the risks and costs associated with trial-and-error field implementation. Moreover, TREECS™-CTS usage can and should be an integral part of the successful administration of ORAP and related range sustainment programs, which can avoid many millions, if not billions, of dollars being lost if operational ranges are closed due to compliance failure.

[10] Personal communication with personnel of the Environmental Chemistry Branch, ERDC

[11] http://www.ncsi.com/tss11/agenda_oacsim.html

9.0 IMPLEMENTATION ISSUES

There are no major implementation issues associated with applying TREECS™ and CTS. Training is helpful and should be conducted for successful use. Installation of TREECS™ on DoD and Army-owned computers requires the System Administrator since it is client based and there are many military security constraints, such as requiring a Certificate of Networthiness (CON) for installed software (TREECS™ has an Army CON). Installation on contractor-owned computers entails much fewer hurdles. CTS is web based; therefore, it only requires establishing a login account for an EPA server. CTS is scheduled to be pushed to a public server during 2017, which will enable much easier access for anyone without an account.

Presently, there are no DoD or Army directives that require the use of TREECS™, and as a result, TREECS™ has not experienced the use that was originally envisioned during its developmental funding. Thus, the benefits of having a powerful forecast modeling tool such as TREECS™ are not being realized. TREECS™ is a mature, validated modeling tool that is fairly easy to apply relatively quickly. Qualified contract environmental personnel could be readily trained for applying TREECS™ and CTS to provide the most expedient and cheapest route to range applications. TREECS™ will not be fully utilized without a requirement for implementation and application. An Army or DoD directive is needed to require such applications, which would provide cost savings, provide much-improved site understanding and alternatives assessment, and help ensure range sustainment.

Predicting the fate of ECs associated with IM explosive formulations presents a unique challenge given that less is known regarding the physicochemical properties of ECs than legacy explosive components. A special effort was made during this project to try to obtain a better understanding of how to properly model ECs. Thus, TREECS™ was applied for laboratory studies of EC fate reported by Dontsova et al. (2014) to expand this understanding. Appendix B of the final report for this project (Dortch et al. 2017) provides the results of these modeling studies and lessons learned for predicting the fate of ECs associated with IM.

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